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PARTICULATE AIR POLLUTANTS RESULTING FROM COMBUSTION

Bernard D. Tebbens, et al

California University
Berkeley, California

21 August 1962

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PARTICULATE AIR POLLUTANTS RESULTING FROM COMBUSTION

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PARTICULATE AIR POLLUTANTS RESULTING FROM COMBUSTION

by

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21 August 1962

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I. INTRODUCTION

The research reported herein is the product of several years' effort to elucidate one aspect of the air pollution problem of urban complexes; namely, the direct contribution of combustion to the complement of exotic organic chemicals in the outdoor atmospheric environment. Most attention has been paid to the complex carbonaceous particulates produced by incomplete combustion, although investigations into gaseous by-products of combustion also have been carried out to a limited extent. Much of the research has been reported in various publications which will be subsequently cited. Work by other investigators along converging lines has been copious. However, since this report is not intended as a review of studies in the field of combustion particulates, the many references to the subject are not necessarily included but may be found in the original accounts from this laboratory.

Exciting findings were made very early in the project undertaking when, during 1955, it was observed that the particulate products of incomplete combustion of several gaseous organic fuels burned in a diffusion flame included polynuclear aromatic hydrocarbons of much greater molecular weight and complexity than the original fuels. The molecular geometry of these by-products was totally different from that of the raw materals--the fuels being various aliphatic hydrocarbons, and the products of interest being aromatic hydrocarbons and some of their partially oxidized derivatives [1]. Organic gases used in the early experiments were natural gas (primarily methane), 1-butene, ethyne, and 1,3-butadiene.* In later studies butane and propane were additional gaseous fuels investigated [2]. Subsequently, several liquid organic fuels were used including hexane, cyclohexane, 1-hexene, toluene, benzene, and low octane gasoline [3]. The same series of polynuclear aromatic hydrocarbons (arenes) was found in the by-products from incomplete diffusion flame combustion of all the fuels,

---

*Chemical nomenclature approved by the I.U.C. Differences (particularly apparent in the figures) reflect diverse editorial policies of journals and/or recently accepted changes.

and the same was true from incineration of such waste products as tree trimmings, paper, and cardboard. Some of the compounds repeatedly found were: anthracene, phenanthrene, fluoranthene, pyrene, dibenz[a,h]anthracene, benzo[a]pyrene, perylene, and coronene.

That these arenes are ubiquitous in contaminated air of urban communities is implied from a variety of atmospheric samples taken in many parts of the world. In Berkeley, for example, a large volume air sample (Figure 1) obtained on a relatively smoggy day contained the same range of polynuclear aromatics as was found directly by combustion. Numerous British analysts have demonstrated the same facts about the air in London--Russian observations in three cities in the Soviet Union, and investigations in Los Angeles have shown the same range of arenes. Almost certainly, air contaminated by carbonaceous smoke from whatever source contains polynuclear aromatic hydrocarbons, though the quantity varies from one community to another as shown by Sawicki, et al. [4].

This phenomenon, herein referred to as "hydrocarbon synthesis in combustion," results from the most widespread contemporary chemical process; namely, oxidation of fuels with atmospheric air for production of heat and power. The extensive use of this process implies that arenes have always been present in smoky air. They will continue to be found until the combustion process is improved to the point where oxidation of carbon is complete, based on criteria far more rigorous than those of current practice.

While the specifics of the mechanism of arene synthesis in combustion have not been investigated in this research project, numerous studies of pyrolysis, and other chemical phenomena, undoubtedly are applicable to the subject. The hypothesis that the arenes are already present in the fuel and are distilled off or rearranged during combustion was rejected early in the study. It is evident that most of the hydrocarbons burned had no such aromatic structure. The very simple aliphatic hydrocarbons represented by methane and propane were primary reactants, just as were the more complex molecules of benzene, cellulose, etc. In other words, so simple a chemical as methane, with a molecular weight of 16, can be the starting material for a product as complex as coronene ($C_{24}H_{12}$), with a molecular weight of 300.

A more likely hypothesis was drawn from various published studies of pyrolysis and petrochemical research [1]. Pyrolytic degradation of

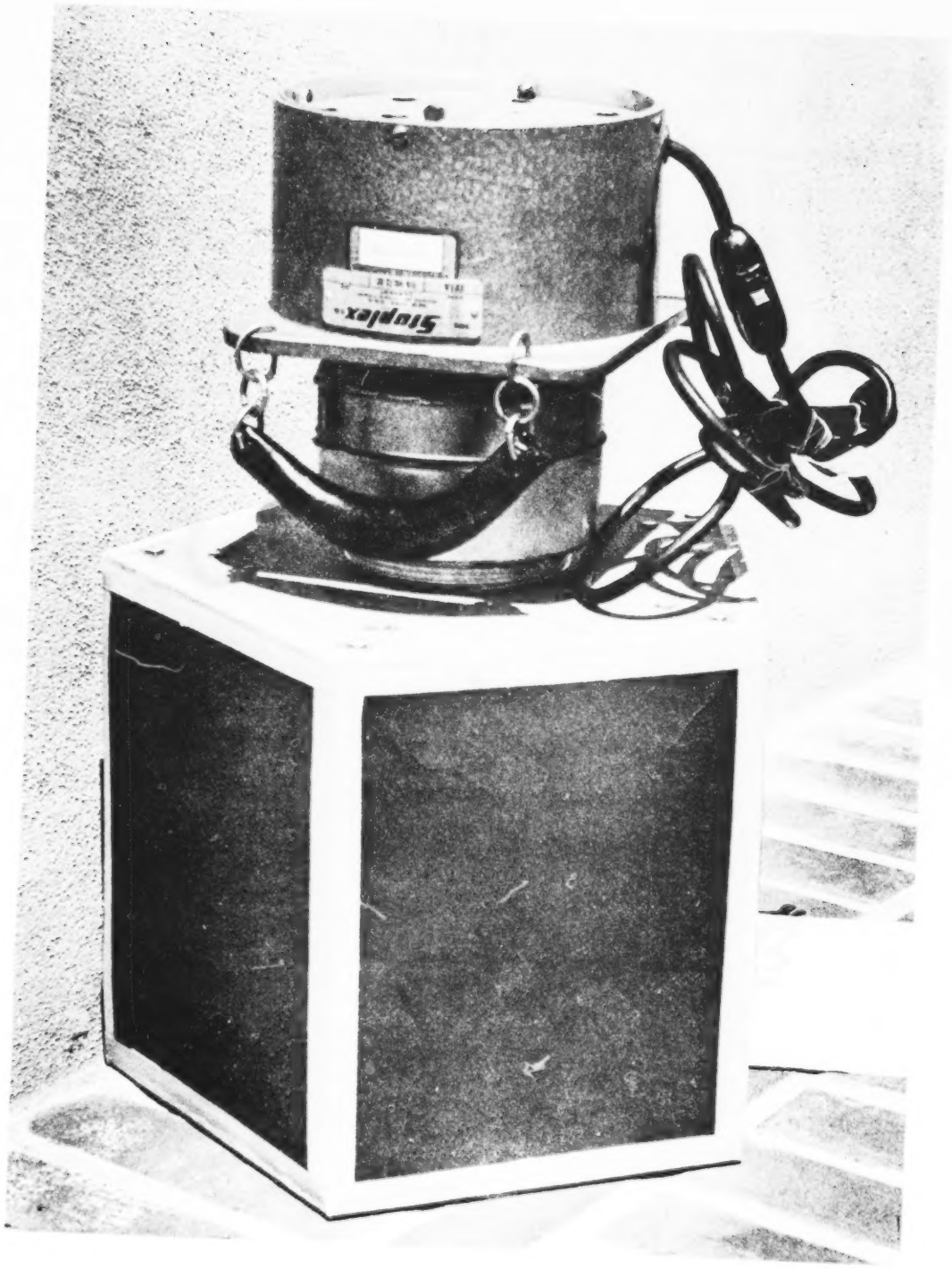


FIGURE I. AIR FILTRATE ON SMOGGY DAY

fuels in the flame results in the formation of hydrocarbons and free radicals of low molecular weight, such as methane, CH_4; methyl, CH_3-; methylene, $-CH_2-$; methylidyne, HC≡; ethene, $H_2C=CH_2$; vinylene, -CH=CH-; ethyne, HC≡CH; and others. These in turn combine to form aromatic structures of great variety. A hypothetical mechanism incorporating this idea is shown in Figure 2, which is adapted from pyrolysis literature. It is important to emphasize that, under ideal thermal and pressure conditions, the yields of aromatic hydrocarbons in pyrolysis may be large, whereas the yields in combustion of fuels are extremely small--only milligrams of aromatics produced per gram mole of organic fuel.

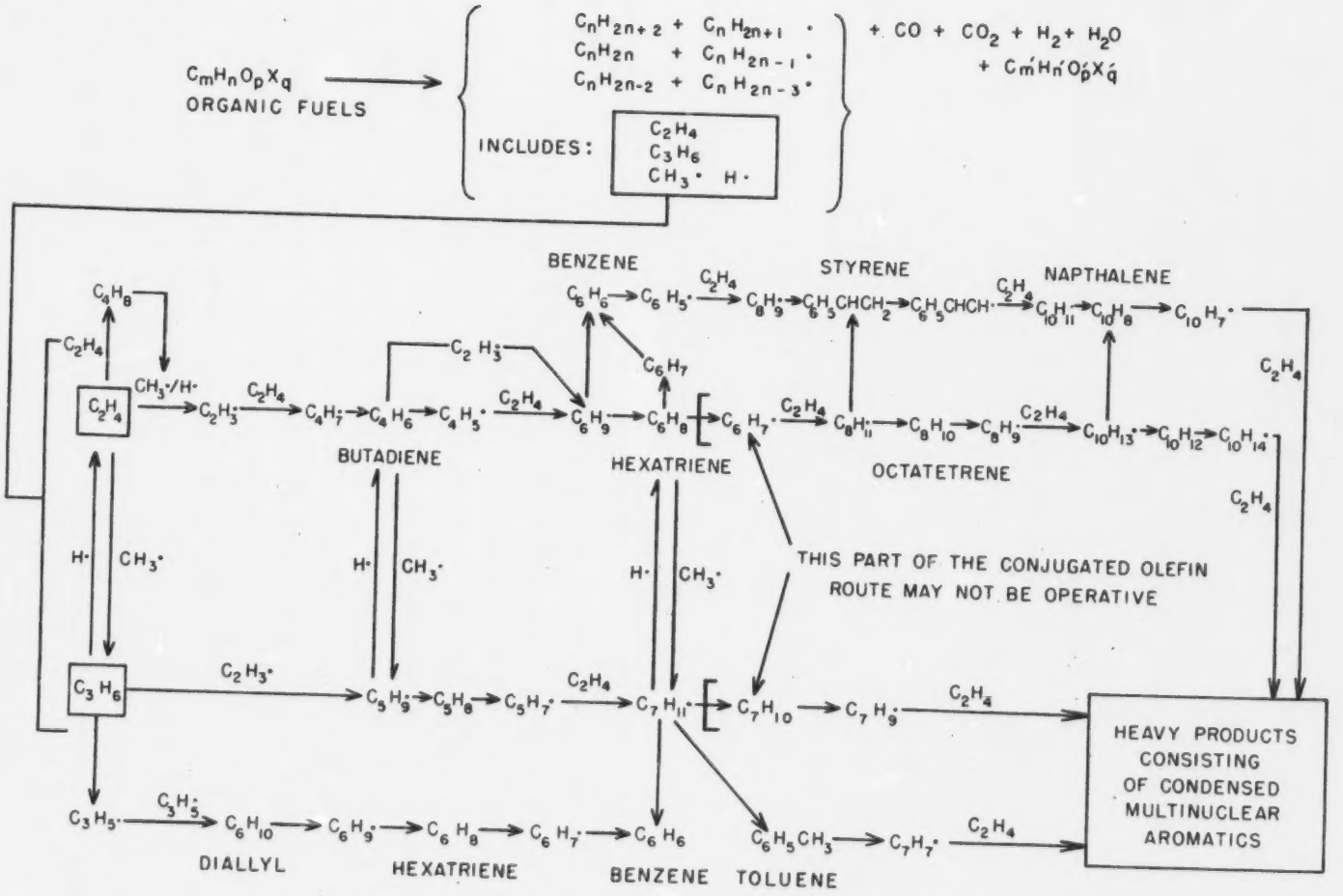


FIGURE 2. HYPOTHETICAL MECHANISM FOR SYNTHESIS OF POLYNUCLEAR AROMATICS FROM COMBUSTION

II. SAMPLING PROCEDURES

Combustion in the laboratory was done in a diffusion flame, utilizing a simple burner so arranged that primary air from a tank of compressed air could be introduced at the combustion source in controlled amounts. Tank air was used to insure absence of particulate contamination in the air supply. From the same source secondary air was fed to the base of the stack which served as a housing for the burner. Air and gaseous fuels were metered.

The system is indicated schematically in Figure 3. Also shown is the system for sampling a portion of the combustion effluent. By means of a pump and meter, up to 1 cu ft/min of the contaminated gases was drawn through a soxhlet extraction thimble for filtration of the black sooty by-product.

Most combustion was conducted to produce black smoke by severely throttling the primary air. Although the several fuels vary widely in their ease of burning, even natural gas, which typically burns clean, could be handled in such a way as to produce a smoky effluent. In all studies of gaseous fuels a control was run to insure that no filterable components were present in the raw combustible material.

Variations in both burning and sampling were introduced from time to time--the former to make possible the combustion of liquid fuels, and the latter to sample certain gaseous by-products. Figure 4 shows the means used to vaporize liquid fuels in order to introduce them in the gas phase to the burner within the stack. The raw liquids were vaporized at temperatures below the cracking point. Provisions for secondary air and for sampling the particulates were previously described.

For estimation of aldehydes from combustion [5], the sampling system was augmented, as indicated in Figure 5, by condensers and refrigerated traps at temperatures of dry ice-acetone mixture. This system was found to be very effective for removing most gaseous components.

Samples from non-laboratory sources were obtained from time to time, always by filtration, to ascertain the polynuclear aromatic content of outdoor air and of effluents from other combustion equipment. Soxhlet

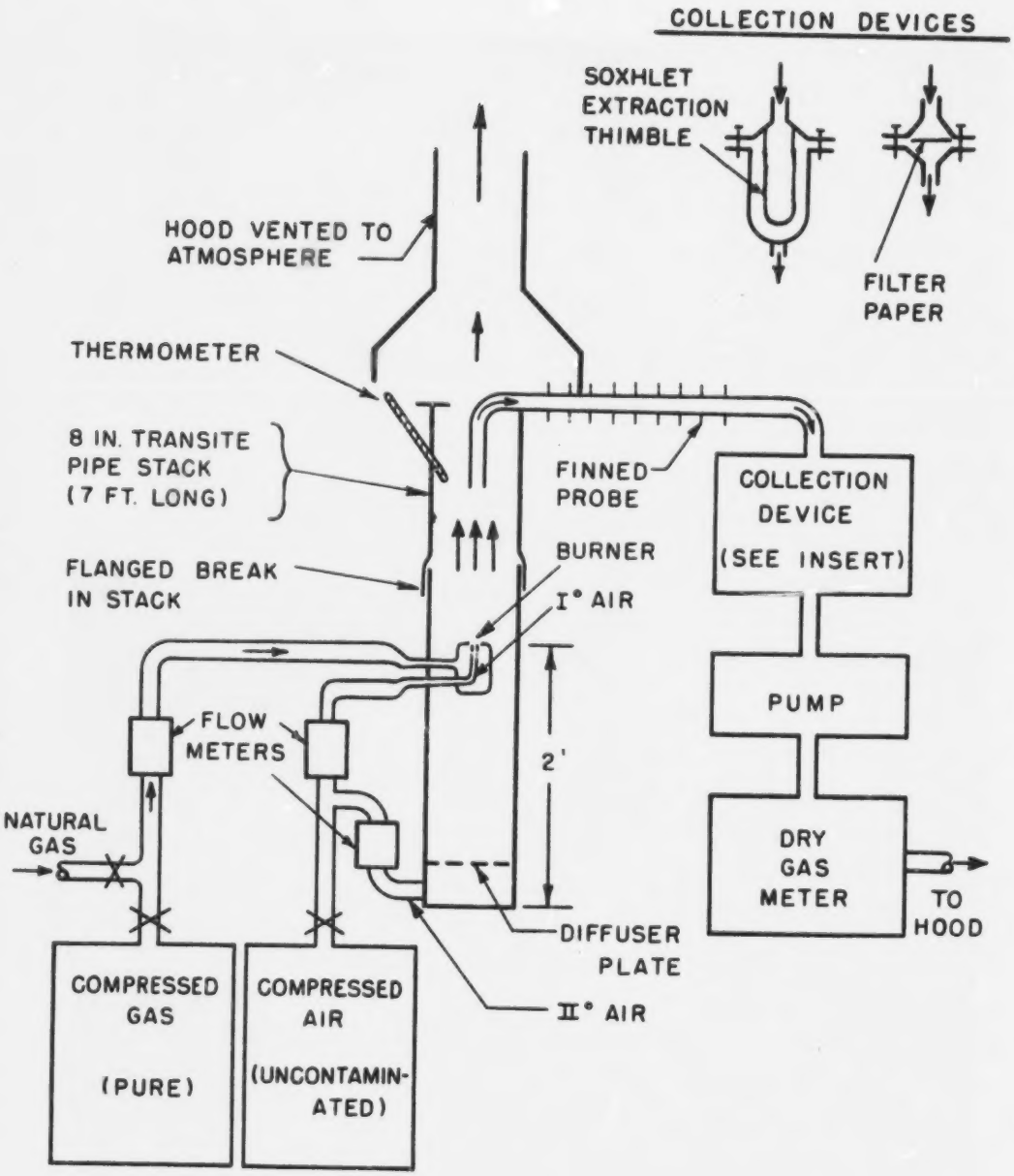


FIGURE 3. SCHEMATIC COMBUSTION AND SAMPLING SYSTEM — PARTICULATES

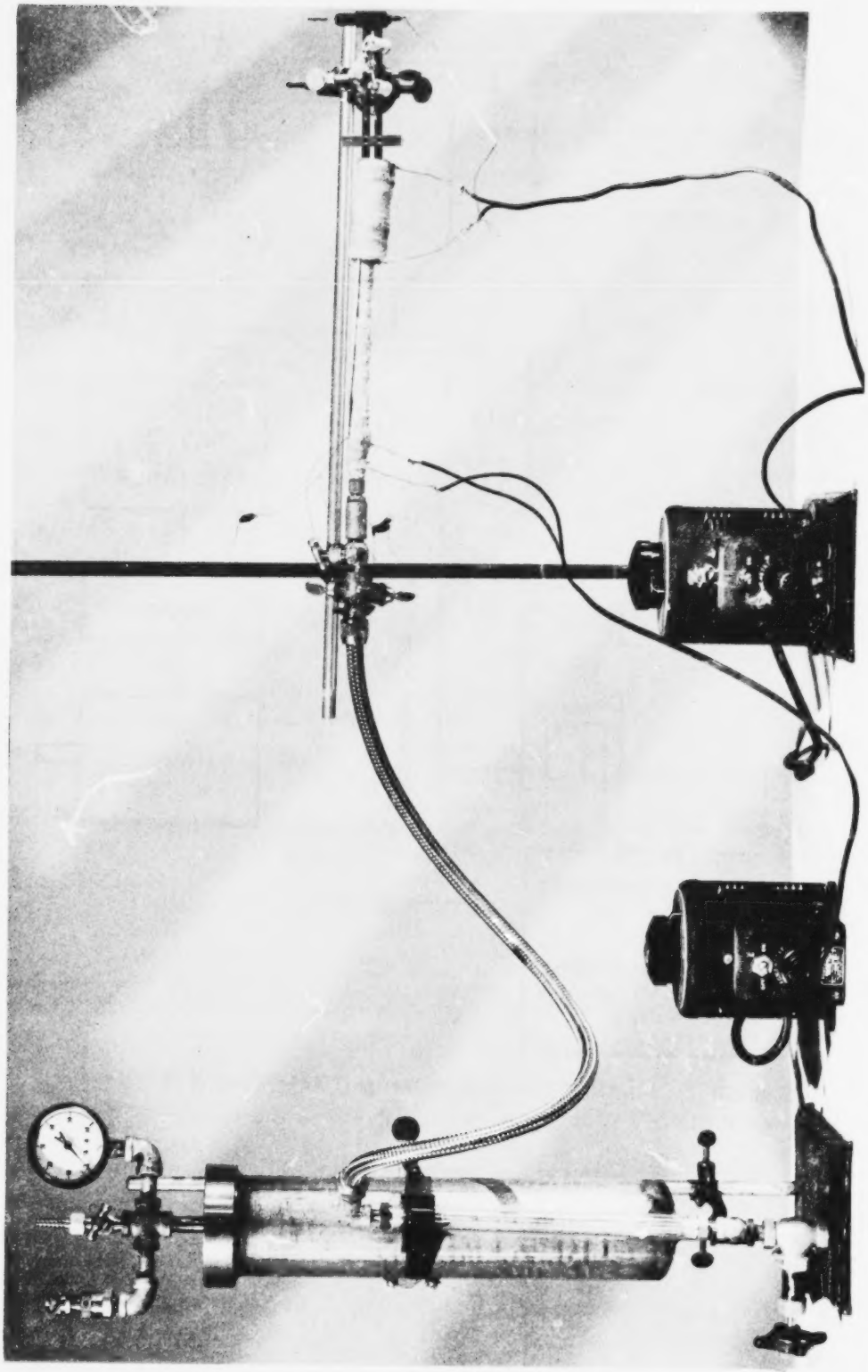


FIGURE 4. BURNER AND PREHEATER FOR LIQUID FUELS

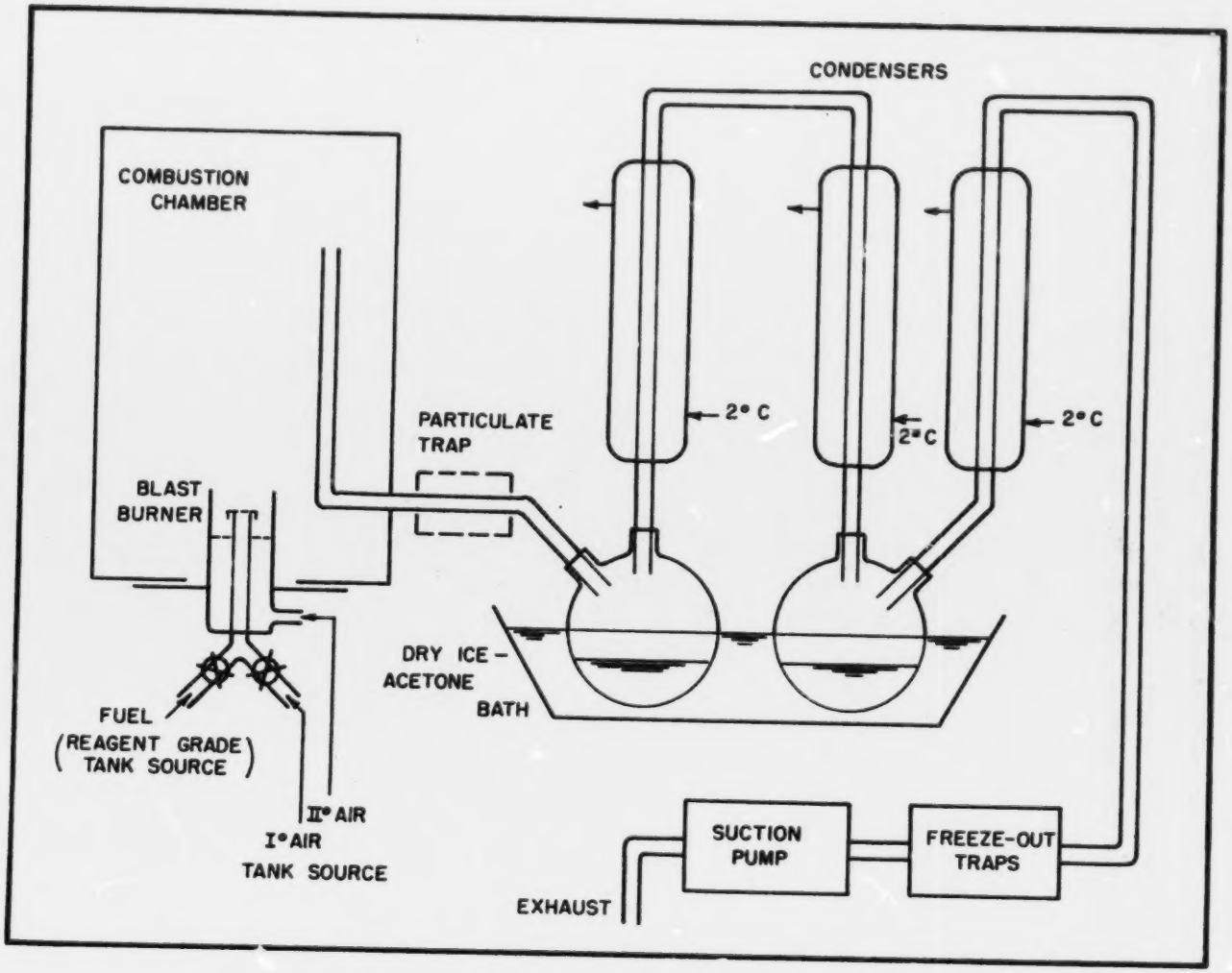


FIGURE 5. SCHEMATIC COMBUSTION AND SAMPLING SYSTEM–GASES

extraction thimbles with appropriate probes were used for automotive emissions and for those from an incinerator burning rubbish. A high volume sampler was used to sample outdoor air, producing (on "smoggy" days) the black filter surfaces shown in Figure 1. It is worth noting that the project was instigated by observations of outdoor air--some filter samples obtained in Berkeley, California in 1953 are described in Reference 6.

III. SEPARATION AND IDENTIFICATION OF POLYNUCLEAR AROMATIC COMPONENTS

Collection of the particulate materials in extraction thimbles was practiced to simplify subsequent analytical procedures. In many cases the approximate weight of collected soot and of subsequently extracted organic compounds was obtained by precise gravimetric techniques. The cellulose character of the filter demanded care in drying the thimble for this procedure. Extraction of organics from the thimble was done by the standard soxhlet reflux method, using diethyl ether as primary solvent to remove from the soot a reddish brown extract which was of oily consistency when the solvent was evaporated. Extraction overnight was the rule. In some cases other solvents were used but were not notably more successful than ether.

After early chromatographic evidence of the presence of a large number of separable components in this extract [1, 2], a separation procedure was evolved [7] which differentiated three classes of the nonvolatile polynuclear aromatic compounds; namely, neutral hydrocarbons, phenolic derivatives, and carboxylic derivatives. This involved successive extractions of the oily residue with dilute NaOH (5%) in which phenolic and carboxylic compounds were soluble, followed by adjusting pH to about 7 with CO_2. In this mixture carboxylic compounds were soluble. The portion insoluble in dilute NaOH solution contained the neutral hydrocarbons. A dilute acid wash (5% HCl) was used for samples suspected of containing basic components. The quality of these separations is indicated by the microcombustion analyses in Table I. Notable is the absence of sulfur- and nitrogen-containing compounds and the appropriate increase in oxygen content of the three classes of components. The presence of oxygen in the neutral hydrocarbon fraction is the result of its content of esters.

Various chromatographic techniques provided the principal means of further separating the fractions. These included paper, column, and gas chromatography, as well as a limited amount of electrophoresis. The earliest approach was by the very simple "Rutter technique" [2] which involves semicircular chromatography on filter circles. Illustrative of

the results is Figure 6, a photograph of the ultraviolet fluorescence of several components from the neutral hydrocarbon fraction. This example shows a similarity of products as indicated by chromatogram patterns from combustion of natural gas, incinerated refuse, a few known compounds, and an outdoor air sample. The similarity of color is not apparent in black and white photographs, but was striking.

TABLE I

ELEMENTAL ANALYSIS OF FRACTIONS FROM 1-BUTENE EFFLUENT

Fraction	Percentage Present				
	Carbon	Hydrogen	Oxygen	Sulfur	Nitrogen
Neutral hydrocarbons	91.2	5.1	3.7	0	0
Phenolic derivatives	81.4	5.7	12.9	0	0
Carboxylic derivatives	70.2	5.2	24.6	0	0

Notable is the fact that several dilutions of acetic acid were used for developing the chromatograms; i.e., 40%, 60%, and 80%. It was found that with increasing acid strength, chromatographic resolution of different arenes was improved, the lower molecular weight compounds being mobile in the more dilute acid with the mobility of higher molecular weight arenes increasing with increasing acid concentration. A hypothetical composite of three chromatograms of a single sample with the three acid strengths and of a group of known arenes is shown in Figure 7. Eighteen components were separable, not all of which could be compared to knowns. Chromatographic data on a group of known arenes together with the color of ultraviolet fluorescence are shown in Table II.

While this technique gave valuable early insight into the variety of chemicals encountered, it was not adequate for the separation of either phenolic or carboxylic fractions, nor did it lead to unequivocal identification of many of the unknowns.

The next steps were the use of two-dimensional chromatography and of paper strip techniques. While primary interest has centered around the neutral hydrocarbon fraction, it is worth noting that strip electrophoresis in dilute NaOH (1%) was found suitable for resolving several carboxylic and phenolic derivatives from their respective fractions, as illustrated

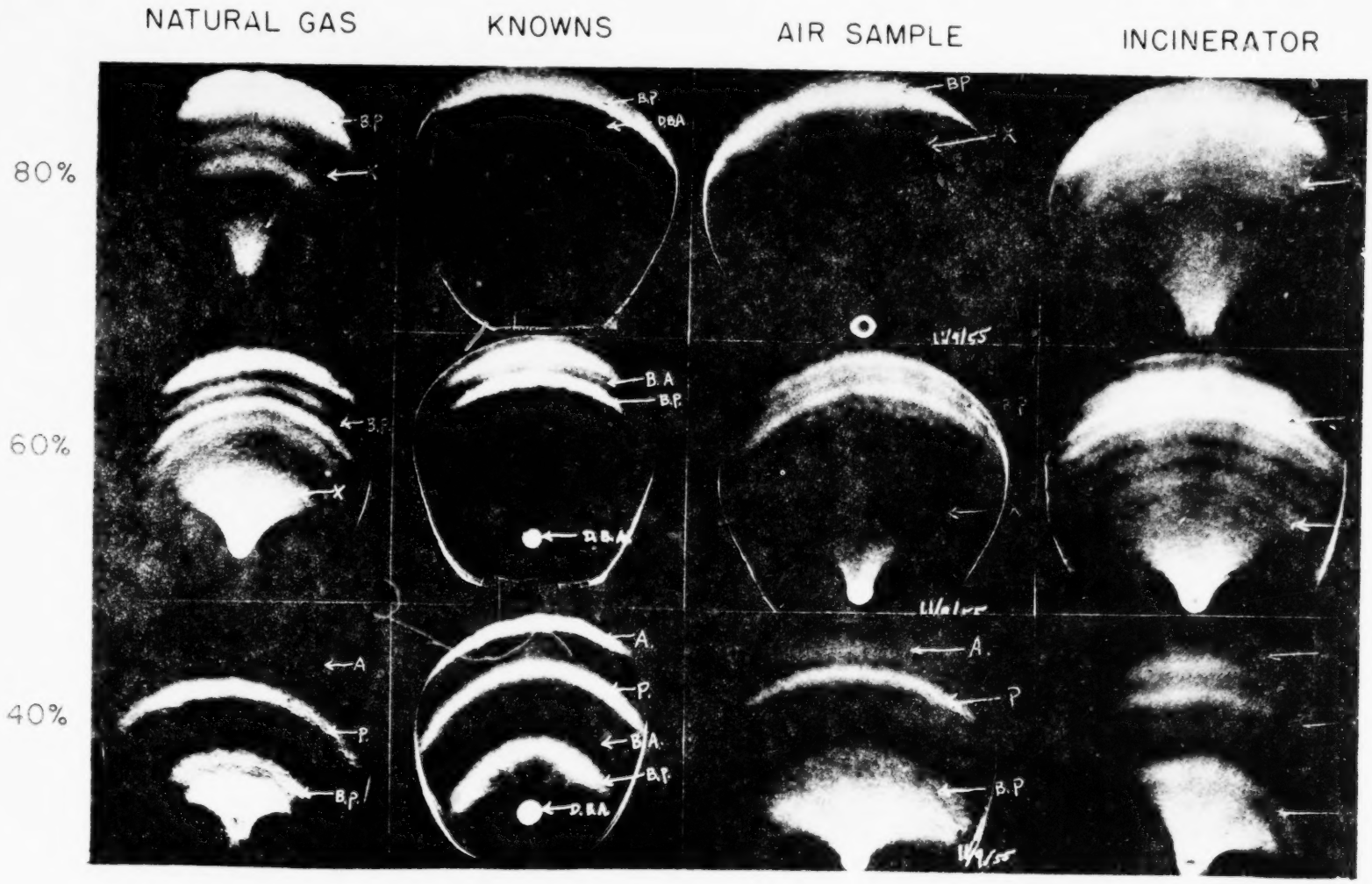


FIGURE 6. CIRCULAR CHROMATOGRAMS OF ARENES FROM COMBUSTION AND FROM OUTDOOR AIR SAMPLE

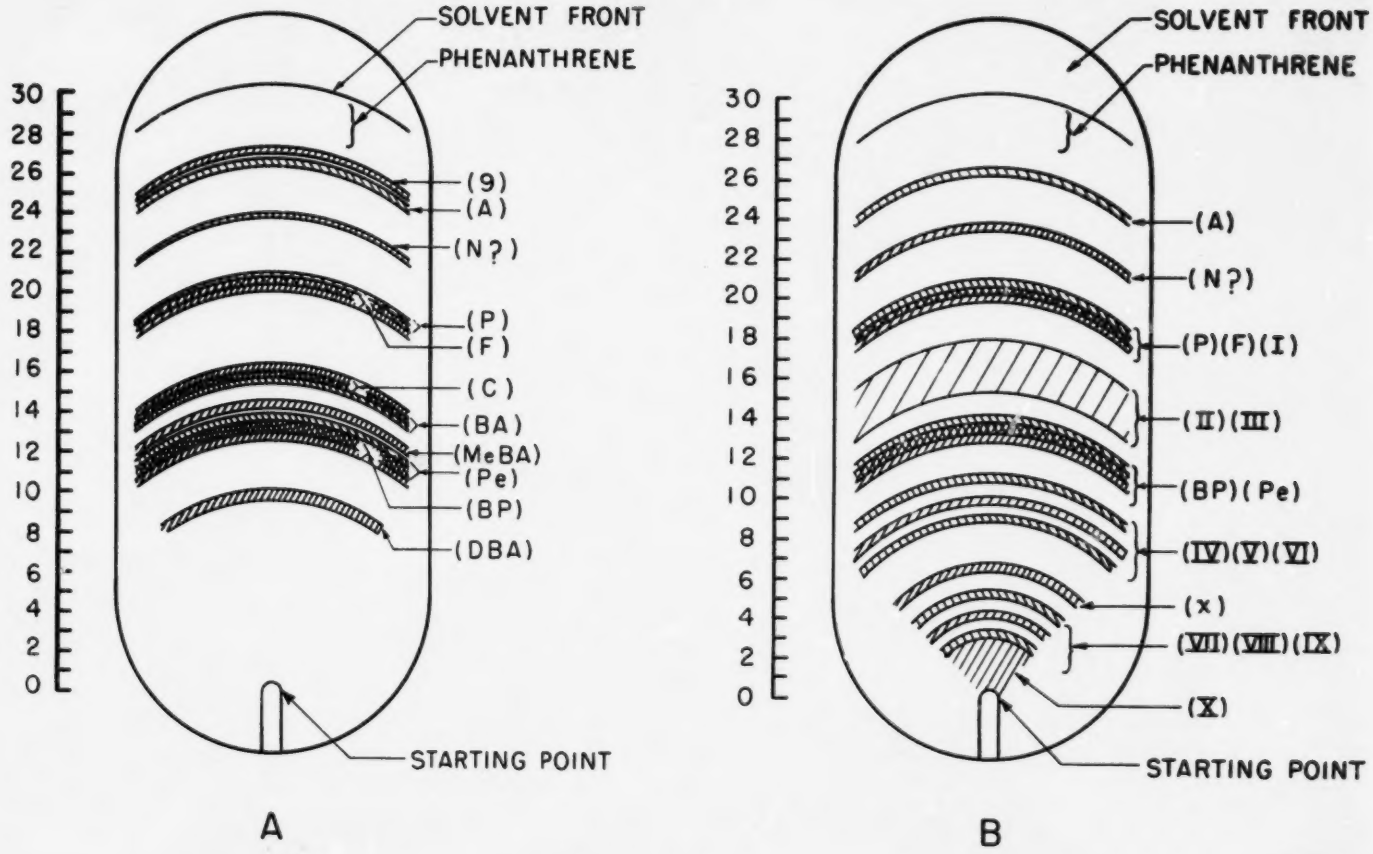
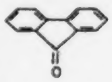
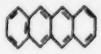
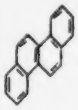


FIGURE 7. HYPOTHETICAL COMPOSITE CHROMATOGRAMS WITH 40%, 60%, AND 80% ACETIC ACID DEVELOPERS A-Arenes of known composition, B-Arenes produced during combustion

TABLE II

COMPARATIVE CHROMATOGRAPHIC AND FLUORESCENT DATA

Compound Name	Formula	(M.W.)	Structure	Fluorescent Color	R_f Values in Acetic Acid Solutions[a]		
					40%	60%	80%
Phenanthrene	$C_{14}H_{10}$	178		Deep violet (pure) Blue (contaminated)	Values cannot be determined because of high volatility.		
9-Fluorenone	$C_{13}H_8O$	180		Brick red	.91	.95	.96
Anthracene	$C_{14}H_{10}$	178		Violet (pure) Greenish blue (contaminated)	.90	.95	.96
Naphthacene[b]	$C_{18}H_{12}$	228		Green (contaminated)	.80(?)	.91(?)	.93(?)
Pyrene	$C_{16}H_{10}$	202		Blue	.71+	.88	.90
Fluoranthene	$C_{16}H_{10}$	202		Grey white	.71	.88	.90
Chrysene	$C_{18}H_{12}$	228		Deep violet	.55	.84	.88
Benz[a]anthracene	$C_{18}H_{12}$	228		Violet blue	.54	.84	.88
9-Methyl-benz[a]antracene	$C_{19}H_{14}$	242		Whitish blue	.49	.83	.84
Perylene	$C_{20}H_{12}$	252		Grey yellow	.47	.82	.84
Benzo[a]pyrene	$C_{20}H_{12}$	252		Blue violet	.40	.81	.84
Dibenz[a,h]anthracene	$C_{22}H_{14}$	278		Yellow green	0	0	.75

[a] Approximate values from circular chromatograms.

[b] Difficult to position because of abnormal behavior.

in Figure 8. Since paper strip chromatography with one per cent NaOH accomplished a resolution of these compounds equally well, as illustrated in Figure 9, electrophoresis was abandoned.

The principal reason for using more sophisticated techniques, including two-dimensional chromatography, was to separate individual components for application of additional identification procedures. In some cases, and especially when dealing with isomers, simple procedures failed to resolve individual components. At one stage of the research, leaching of a particular chromatographed spot from a large number of replicate paper chromatograms was tried in an effort to obtain enough of any one compound in ether, or other solvent solution, to apply ultraviolet absorption, or other spectroscopy, to dilute solutions. Since this procedure was both time-consuming and tedious, a more feasible technique was developed--that of cutting the desired spot from one chromatogram and using the paper as a suspending medium for spectroscopy.

A small strip of the chromatogram containing the compound under investigation was placed in an adapter fitted to the conventional cell holder of the Beckman Model DU spectrophotometer which had a photomultiplier attachment. The paper strip was held in position in the cell holder by replacing the cuvette with a small wooden block of the same dimensions split down the middle to receive the paper. A drilled hole replaced the normal window aperture.

Experiments with polynuclear aromatic hydrocarbons of known composition indicated that the amount of material necessary to obtain ultraviolet absorption curves by this method was approximately 1 to 10 micrograms in a spot not exceeding one inch in diameter. Figure 10 shows the ultraviolet absorption curves of some tentatively identified compounds compared to compounds of known composition. At this point no quantitative estimation of a compound could be obtained from either absorption curve or fluorescent intensity. Various modifications of the strip holder and of the spectrophotometer optics did not significantly improve the quantitative possibilities of the method, though they did increase somewhat the resolution of absorption bands for qualitative purposes.

Although gas chromatography was tried at an early stage of its development, the low vapor pressure of the chemicals of principal interest appeared to limit the possible application of this procedure. The recent use of higher operating temperatures and greater sensitivity have increased

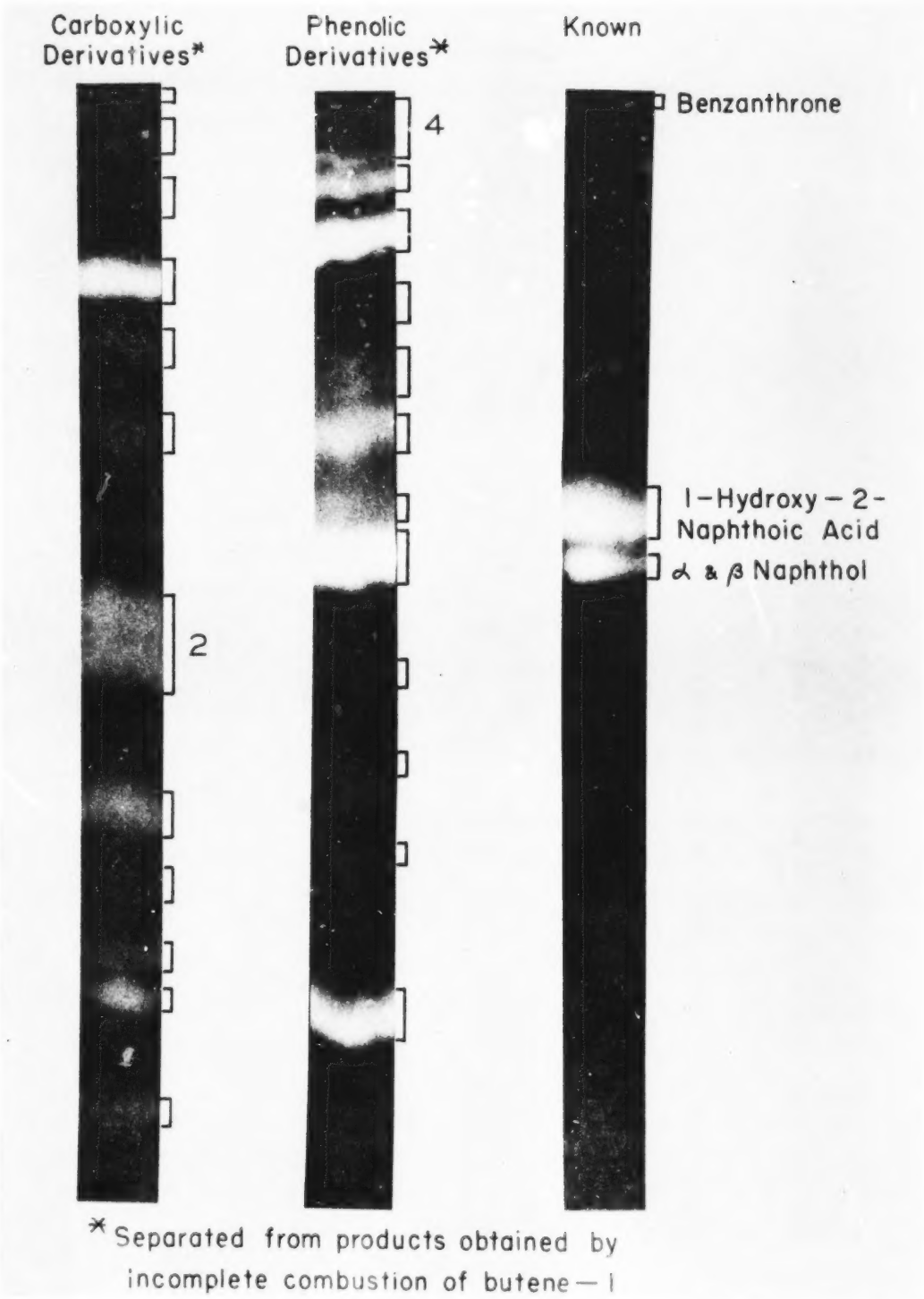


FIGURE 8. ELECTROPHORETIC SEPARATION OF PRODUCTS FROM INCOMPLETE COMBUSTION

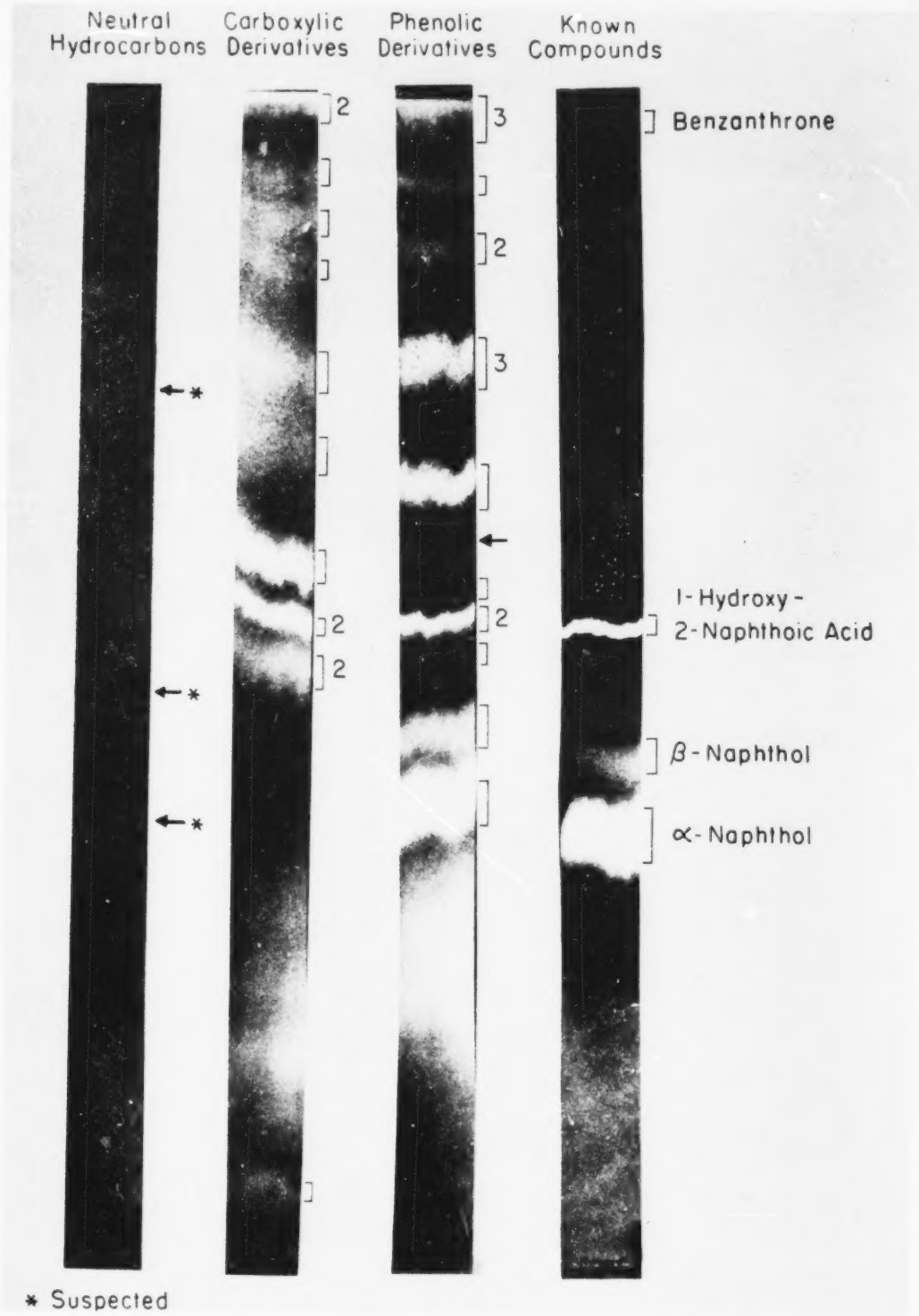


FIGURE 9. DESCENDING STRIP CHROMATOGRAMS OF PRODUCTS FROM INCOMPLETE COMBUSTION

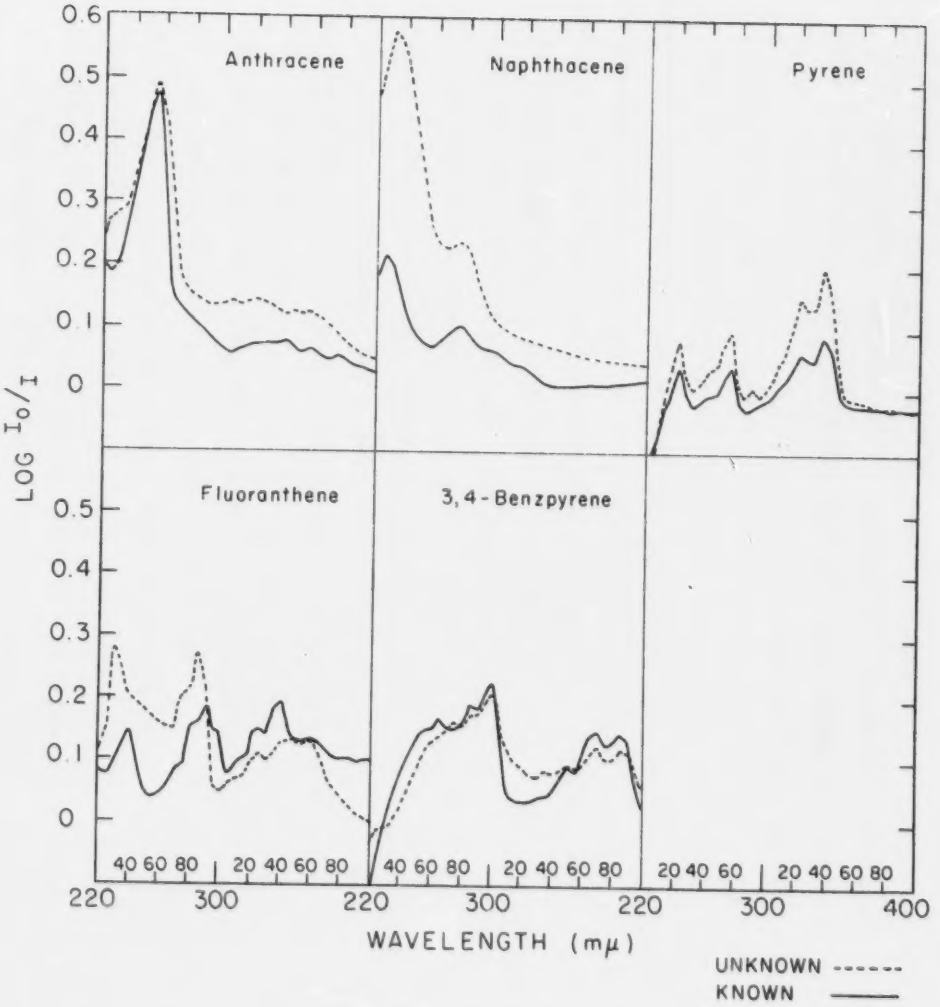


FIGURE 10. ULTRAVIOLET ABSORPTION CURVES OF KNOWNS AND UNKNOWNS

its potential, though it has not yet been exploited. Column chromatography with various solvents proved itself of some value in separating groups of compounds, but resolution of isomers, and in some cases of nonisomers, required an excessive number of time-consuming refractionations. For the most part, modifications of paper chromatographic techniques have been of the greatest value in this research.

As indicated, the comparison of R_f values in chromatography and comparison of fluorescent colors to those of known compounds was useful in preliminary identification of a number of the arenes. Subsequent ultraviolet spectroscopy contributed to the identification, but did not always attain the desired sharpness of resolution.

Since it appeared useful to separate larger than microgram quantities of the arenes for purposes of quantitation, identification, and possible biologic experiments, fractional sublimation of the low vapor pressure organic compounds was attempted as a method of separating single components. This technique involved a low pressure and elevated temperature to encourage vaporization of the relatively nonvolatile arenes from a weighed quantity of the mixture contained in an alundum boat. An electrically heated furnace and a cooling jacket were constructed to fit around a sublimation tube in such a way that both heater and cooling device could be placed at appropriate positions along the length of the tube. The schematic drawing of this system is shown in Figure 11. By careful adjustment of both temperatures, an almost linear thermal gradient could be achieved along the sublimation tube. Pressure regulation in the system was achieved by use of a vacuum pump and a needle valve; the latter acting as a slow leak for pressure maintenance. It was found that pressures between 5.0 and 0.01 mm of mercury were satisfactory, since within that range the temperature of the system appeared to control the rate of sublimation. All pressures below 1.0 mm were determined with a Pirani vacuum gage; a McLeod gage was used above 1 mm. More details of the system are available in Reference 8.

Using a mixture of known arenes, including anthracene, pyrene, benzo[a]pyrene, and dibenz[a,h]anthracene, the system was found suitable for separating the materials when appropriately repeated. As shown in Sample A of Figure 12, a first separation left anthracene and pyrene still mixed, with benzo[a]pyrene and dibenz[a,h]anthracene reasonably well separated in a series of fractions. Subsequent treatment of the anthracene and pyrene mixture, as shown in B, Figure 12, also led to their further

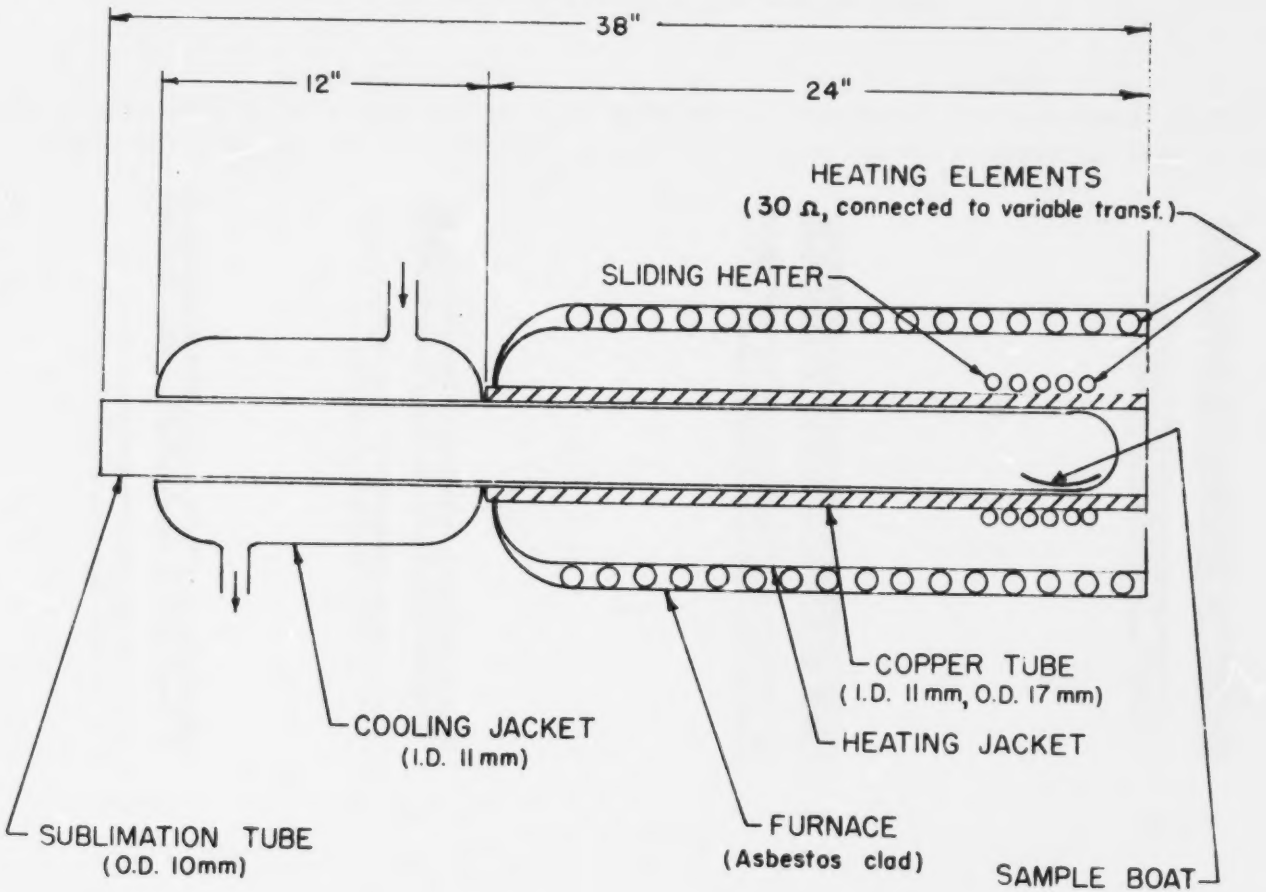


FIGURE II. SCHEMATIC FRACTIONAL SUBLIMATION APPARATUS

W. Photographs taken under white light

UV. Corresponding photography taken under short wave length ultraviolet light

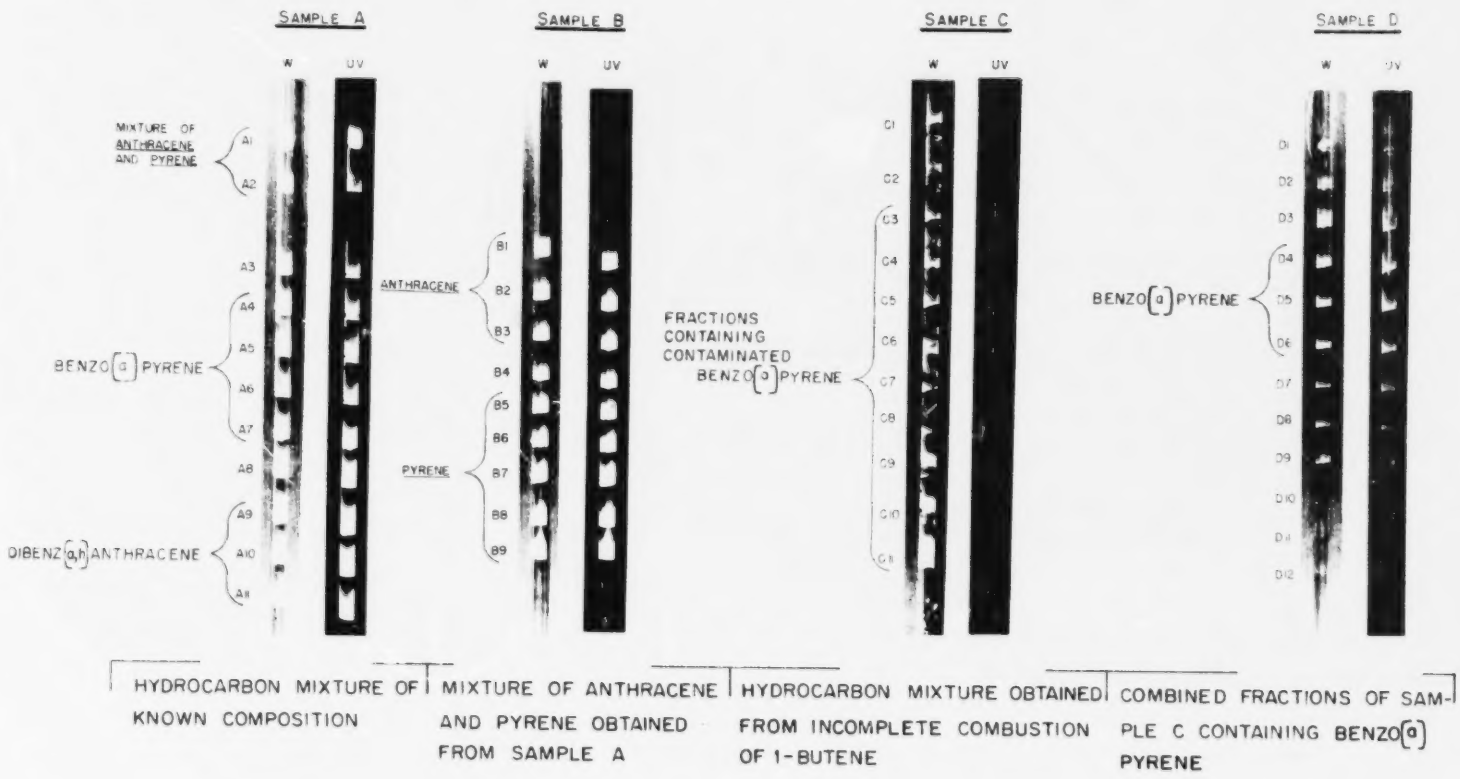


FIGURE 12. SEPARATION OF KNOWN MIXTURES IN SUBLIMATION TUBES

separation in a series of fractions. After such fractionations, a semi-quantitative determination of single components was possible by cutting and weighing appropriate sections of the sublimation tube. The given arene in a section of tube could be removed from it in a solvent to make it available for further identification and other use.

When an unknown mixed sample of the hydrocarbon fraction (obtained by preliminary separation of the products of incomplete combustion of 1-butene) was treated in the same manner, clear-cut separation of fractions was hindered by the presence of a resinous component which could not be moved quantitatively in the sublimation system. This resin appeared to be a series of homologous or vinylogous compounds, the majority of which had a very high molecular weight and which remained as a residue in the sublimation boat. For the intended use of the procedure, only extensively repeated fractionations were successful in purefying the aromatic hydrocarbons contaminated with this material. The resin quenched almost all fluorescence as indicated in samples C and D of Figure 12, and it had to be removed before identification procedures were applicable. Although in theory the sublimation technique with pure compounds was potentially useful, actual use of the method for arenes resulting from combustion was severely limited by this resinous material. While this same resin might also have interfered with chromatography, it was found to be slightly more mobile than anthracene in the developers used so that it moved forward with the solvent front in typical chromatographic procedures. The suitability of sublimation could be increased by finding a way to remove interfering materials.

IV. FLUORESCENT SPECTROSCOPY

Fluorescent analysis has been found in our experience, as well as that of other investigators, to be the most valuable tool for both identification and quantitation of arenes. Most of the organics of interest in this research fluoresce with high intensity. The spectrum of the fluorescence itself is characteristic of individual compounds, and since intensity of fluorescence can be measured with appropriate instrumentation, quantitative estimates of the amounts of separated materials can also be made.

A system was devised utilizing a modified Beckman Model DK-2 spectrophotometer to which was added an additional monochromator and energy source; the fluorescent energy was recorded on a chart coupled with the wave length drive of the instrument. This system plotted wave lengths in millimicrons (mμ) against the fluorescent energy. A special adapter, illustrated in Figure 13, was made to accommodate paper strip chromatograms. By careful selection of the ultraviolet irradiation source for producing the fluorescence and of ultraviolet filters in the system to eliminate that source energy from reaching the detector, very good fluorescent spectra have been recorded with both knowns and unknowns. More details of the system may be found in Reference 9.

For qualitative information on arenes, the mixtures were first separated by paper chromatographic techniques with the starting material located in a narrow straight line or a circular spot. The amount of material found most desirable for analysis was a few micrograms in a circular spot of about 2 cm-diameter or in a narrow band. Although compression of the paper on which the material was located (20,000 psi) increased the fluorescent efficiency by about 10%, this was not found to be a necessary part of the procedure. Figure 14 illustrates the very close correspondence in fluorescent curves between a number of arenes of known composition and components separated from by-products of poor combustion. In solution these components either fluoresced differently or without the good resolution obtained when paper was used as the suspending medium. This is illustrated for pyrene, which is E of Figure 14, and for coronene, H.

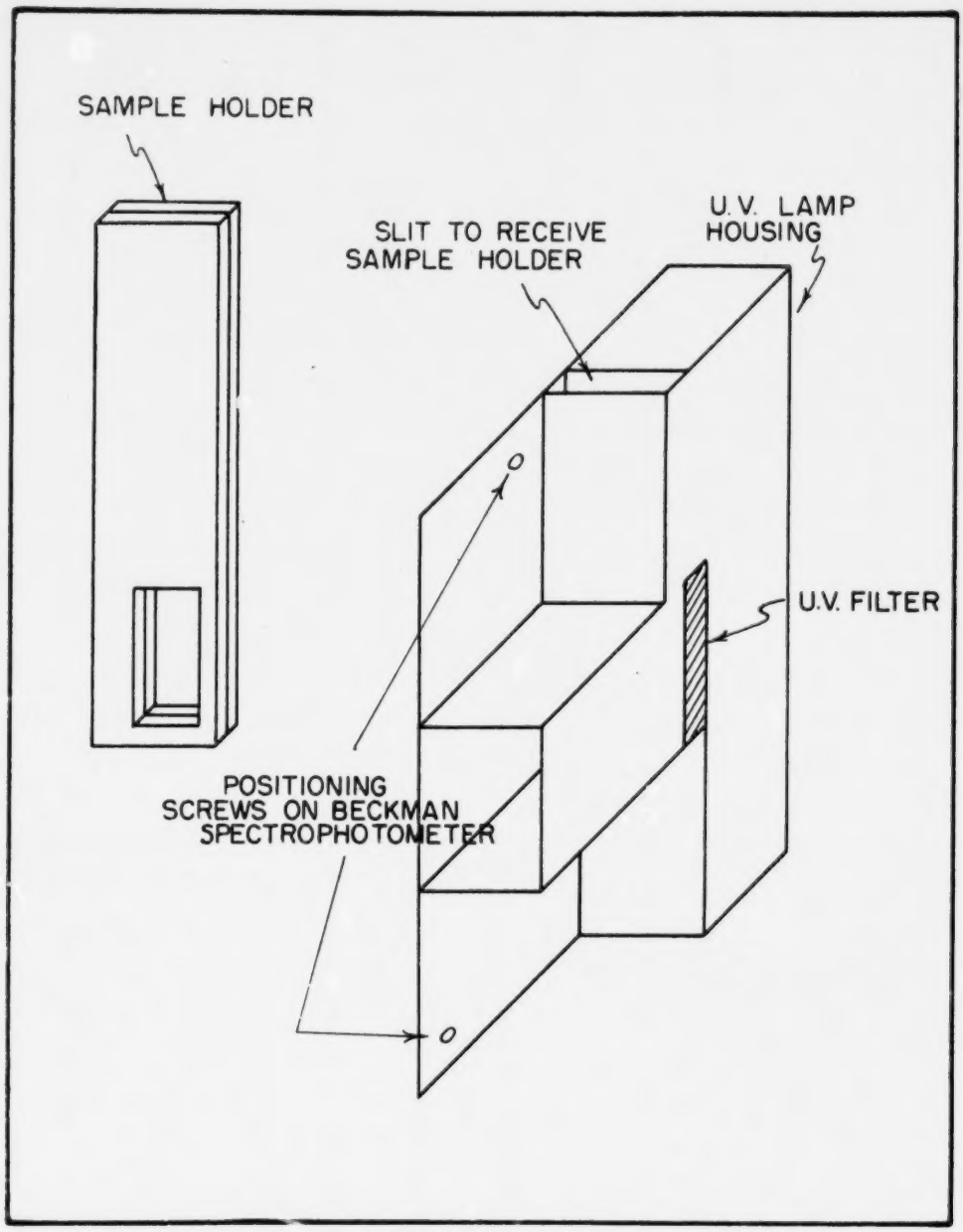


FIGURE 13. SCHEMATIC SAMPLE HOLDER AND MERCURY LAMP HOUSING FOR FLUORESCENT SPECTROSCOPY

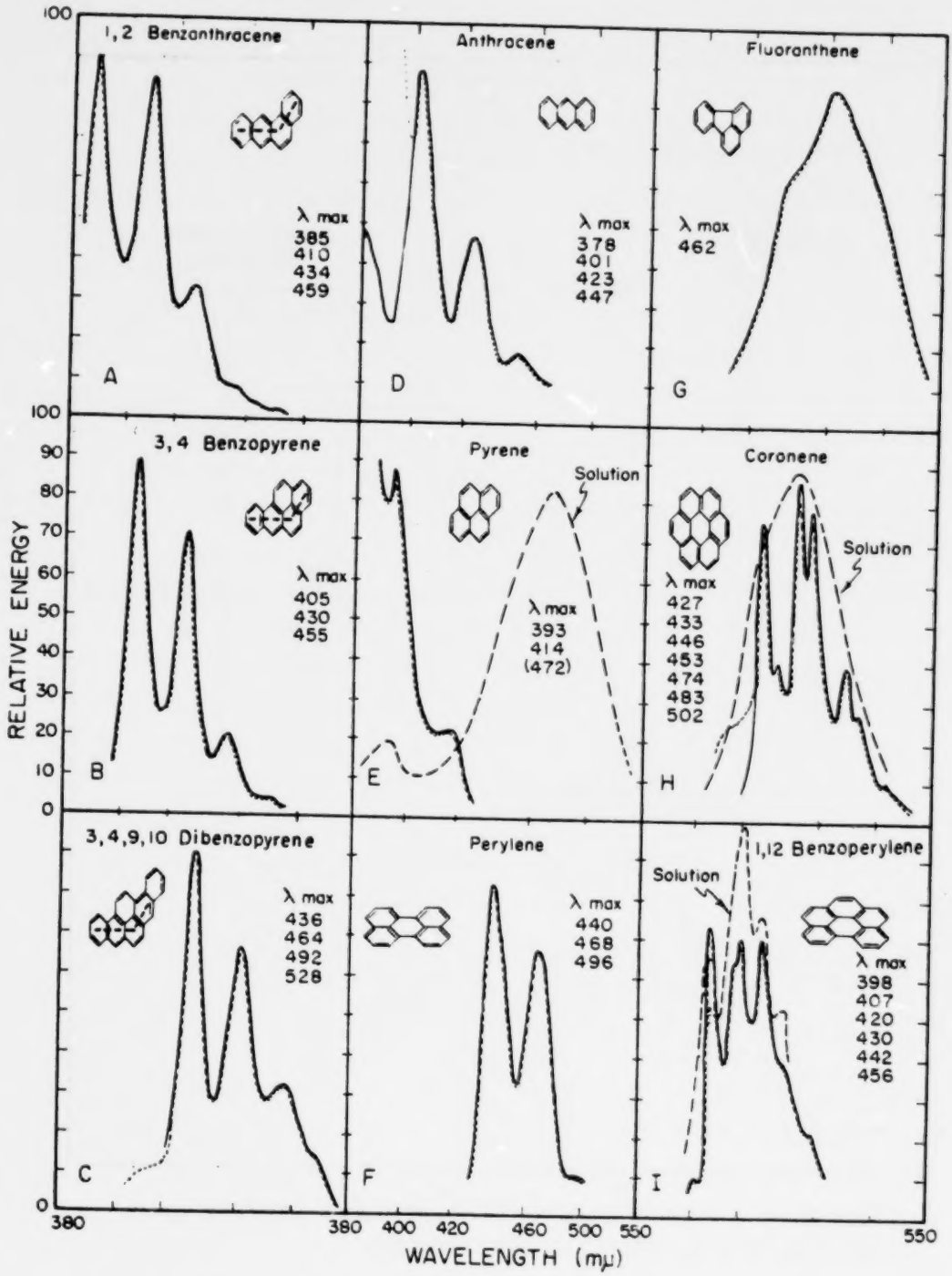


FIGURE 14. MATCHING FLUORESCENT CURVES OF ARENES FROM KNOWNS AND EXPERIMENTAL SAMPLES

It is possible to identify a number of arenes resulting from combustion by the correspondence of peaks of maximum fluorescent intensity with those of knowns. Also, it is interesting to note that the presence of several arenes was not indicated by this technique. Figure 15 shows fluorescent spectra of nine such compounds, including chrysene; benzo[e]-pyrene; dibenz[a,h]anthracene; and others. On the other hand, Figure 16 shows fluorescent curves of nine unknown components which have not been identified due to the lack of comparison fluorescent spectra from knowns. With known compounds for comparison there seems no reason to doubt that a combination of chromatography and fluorescent analysis would offer an excellent means for positive identification of these hydrocarbons. It should be noted that a few aromatics, such as naphthacene and pentacene, have a low quantum efficiency, and, therefore, their identification by these techniques is not possible.

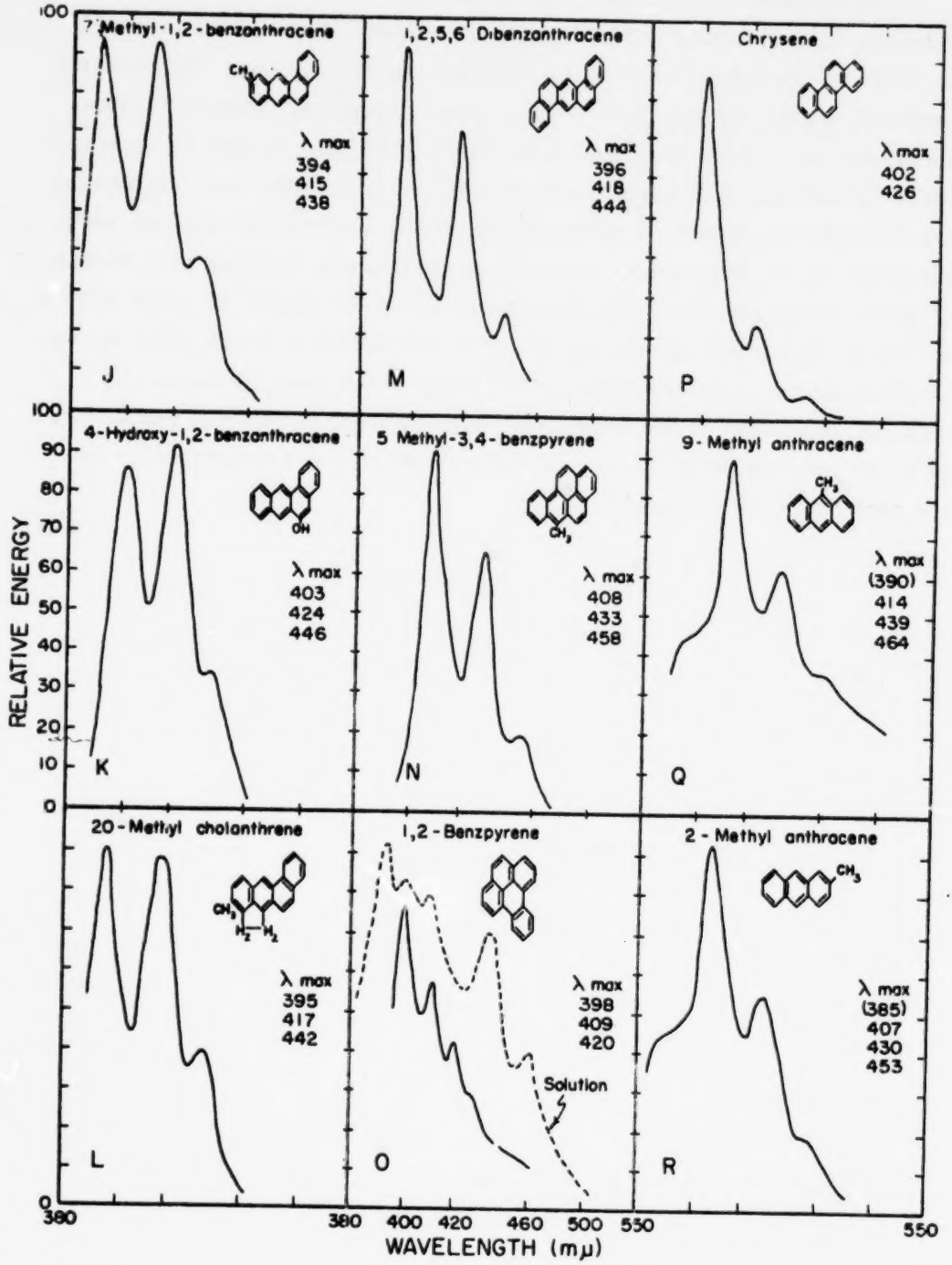


FIGURE 15. FLUORESCENT CURVES OF KNOWN ARENES NOT MATCHED IN EXPERIMENTAL SAMPLES

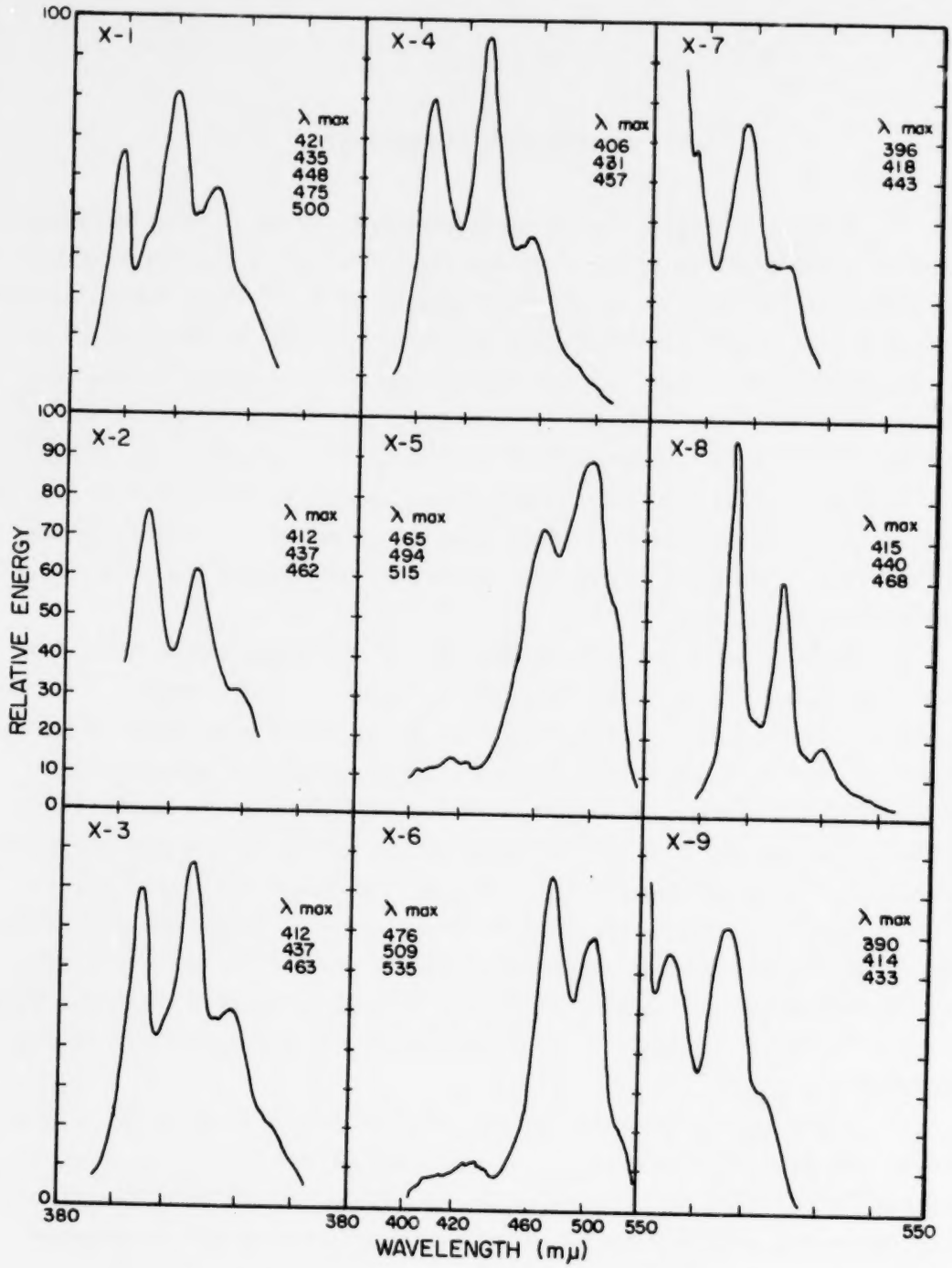


FIGURE 16. FLUORESCENT CURVES OF UNKNOWNS FROM EXPERIMENTAL SAMPLES

V. QUANTITATIVE FLUORESCENCE

Figure 17 shows a series of fluorescent curves of various quantities of benzo[a]pyrene prepared on the previously described instrument. By measuring the distance between the maximum of the peak at 405 mμ to the trough at 421 mμ and plotting those distances as shown in the figure, a linear relationship was noted between the amount of material in the chromatographed spot and the height of the peak. This measurement then constituted a quantitative estimate of the amount of benzo[a]pyrene within the limits of about 0.01 and 0.5 micrograms (μg). In practice, the measurement was considered satisfactory between 0.1 and 0.5 μg of micrograms of material. Comparable quantitative results were obtained with a number of other hydrocarbons.

Several important limitations of this technique were noted. The most significant is that many fluorescent compounds prove sensitive to ultraviolet light. As a result, there was an appreciable decrease in instrument response as these materials were exposed repeatedly to radiation. Figure 18, for example, illustrates the effect of exposure sensitivity in reducing the height of the peak when a single sample was run several times through the same spectrophotometer program. With benzo[a]pyrene the effect was probably due to the irradiation of the spectrophotometer itself; while for anthracene the additional effect of volatilization of the compound may have contributed to successive reductions of peak maximum. This difficulty was overcome by using only freshly prepared chromatograms for quantitative analysis.

The second problem encountered was the self-absorption of fluorescence when an excessive quantity of material was present in the paper chromatogram. This self-quenching led to loss of linearity of the fluorescent energy output above about 0.5 μg of material in a 2 cm-diameter spot.

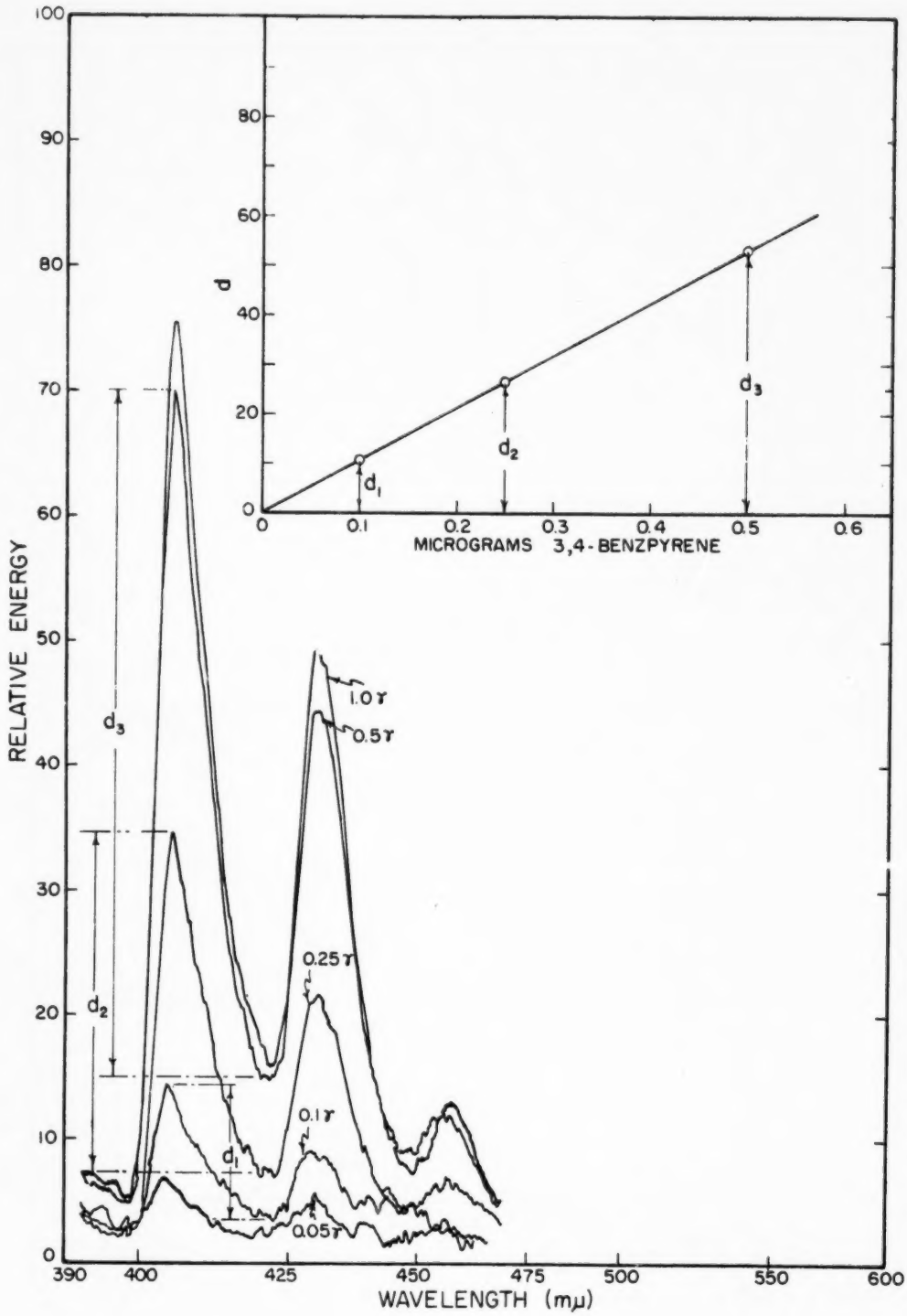


FIGURE 17. FLUORESCENT CURVES FOR QUANTITATION OF BENZO [a] PYRENE

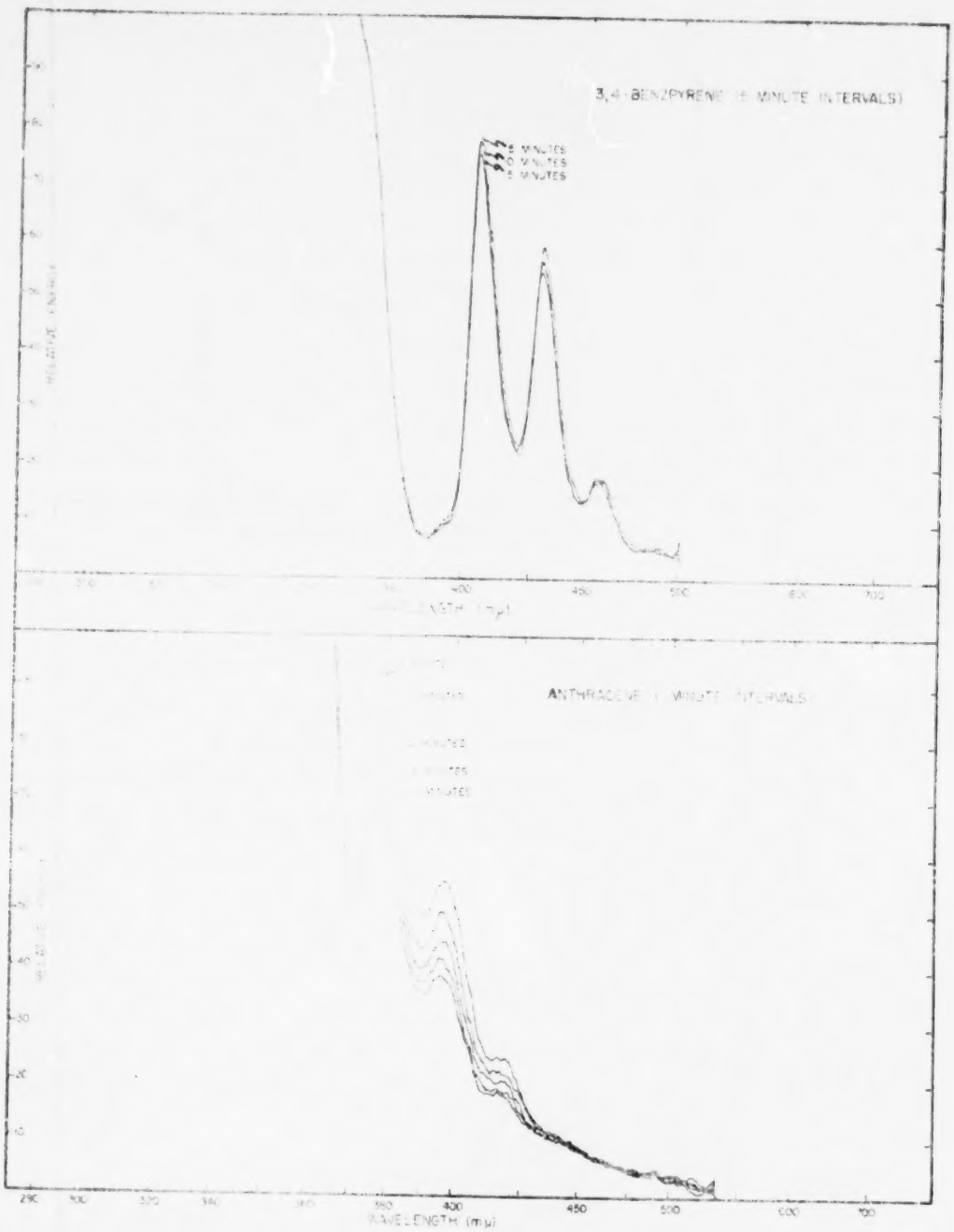


FIGURE 18. FLUORESCENT CURVES – EFFECT OF REPEATED PROGRAMMED ULTRAVIOLET IRRADIATION IN SPECTROFLUOROMETER

VI. QUANTITATIVE SPECTROFLUOROMETRY

In a yet unpublished study (to be included in Monograph No. 9 of the National Cancer Institute), attention was given to the theory of quantitative spectrofluorometry because of its obvious value in this field of experimentation. A relationship among intensity of incident monochromatic radiation, conversion to fluorescent energy of a given wavelength, absorption of both incident and fluorescent energy, and the geometry of the instrumental system was derived to explain some of the non-uniformity of quantitative results of different investigators. The mathematical expression developed for a completely collimated system with fluorescence measured at right angles to the monochromatic incident radiation was checked experimentally within a range where Beer's law holds with anthracene, benzo[a]pyrene, and perylene. For very dilute solutions, the expression is simplified to a linear relationship between concentration and fluorescent energy. The general expression is:

$$I_{F_{\lambda_1}} = \int_{y_1}^{y_2} \int_{x_1}^{x_2} I_{o_{\lambda_o}} P_{\lambda_1} k_o c e^{-k_o c x} e^{-k_1 c y} \, dx dy$$

where

$I_{F_{\lambda_1}}$ = fluorescent intensity at wavelength λ_1 at right angles to incident intensity.

$I_{o_{\lambda_o}}$ = incident ultraviolet intensity at wavelength λ_o.

P_{λ_1} = conversion constant, incident energy to fluorescent energy.

k_o, k_1 = absorption coefficients at specified wavelengths (l/mol cm).

c = molar concentration of fluorescent material.

x_1 to x_2 = width of exit slit (cm).

y_1 to y_2 = width of entrance slit (cm).

VII. IDENTIFICATION OF ALDEHYDES

In almost the only experimentation which involved gaseous as well as particulate effluents from combustion of fuels, a quantitative and qualitative method for aldehyde analysis was evolved [10]. The technique was applied to aldehydes whether adsorbed on particulate material from combustion or collected by condensation and absorption. The procedure included the formation of a precipitated crystalline bis-methone derivative by adding 5,5-dimethyl-1,3-cyclohexanedione (2% in alkaline solution) to a collected sample in an amount not exceeding its solubility when the solution was later acidified. With aldehyde concentration of about 100 μg/ml, and after appropriate digestion and crystallization, the recovery of known amounts of several aldehydes was 30 to 50%. Formaldehyde, however, was recovered quantitatively.

On dehydration the crystalline bis-methone derivative was converted to a xanthene derivative. Both the methone and the xanthene derivatives of aldehydes have specific melting points which are clearly different for different aldehyde compounds as shown in Table III. The crystalline forms of the various derivatives are distinctive, and infrared spectroscopy further identifies individual compounds.

The fractional sublimation technique previously described was more useful when applied to these aldehyde derivatives than to the arenes. Mixtures of the derivatives could be separated quantitatively by the technique; and since the derivatives had a much larger molecular weight than the aldehydes themselves, their gravimetric estimation was possible. Experimentation with aldehydes was simplified by the fact that only a single aldehyde (formaldehyde) was isolated from the combustion samples, whether the combustion was complete or incomplete.

TABLE III

MELTING POINTS OF ALDEHYDE DERIVATIVES

Aldehyde	Melting Point, °C	
	Bis-Methone Derivative	Xanthene Derivative
Formaldehyde	191-192	172-173
Acetaldehyde[a]	141-142	176.5-177
Propionaldehyde[a]	157-158	142-143
Butyraldehyde[a]	134-135	135-135.5
Isobutyraldehyde[a]	153-155	155-156
Valeraldehyde	107-109	---
Isovaleraldehyde	154-155	---
Hexanaldehyde[b]	101-103	---
Benzaldehyde[a]	194-195	204-206
Crotonaldehyde	[c]	---
Acrolein	190-192	---
Aldol	70-80[d]	---
Glyoxal	185-190	---
Furfural	147-149	---
Pyruvic aldehyde[e]	---	---
Phenylacetaldehyde	164-165	---

[a]Readily converted to xanthene derivatives.

[b]Limited solubility in water limits yield of bis-methone derivative.

[c]Apparent decomposition of derivative above 130°C.

[d]Uncertain.

[e]Does not form bis-methone derivative.

VIII. DISCUSSION

The analytical techniques applied to the by-products of combustion and to some atmospheric samples have varied during the course of this research program. There occurred a gradual evolution of increasingly sophisticated techniques as available instrumentation, and understanding of the complex character of materials, developed. As indicated, the originally published articles contain details of analysis not considered pertinent to this summarization. The difference between the purely qualitative observations of circular paper chromatography, illustrated in Figure 6, and the quantitative estimation of the same compounds by flucrescent analysis, illustrated in Figure 17, is enormous. The latter technique and our adaptation of paper chromatograms to it were developed into a useful procedure only during the course of this project.

Only the simplest of separation techniques were necessary to demonstrate the large range of particulate organics produced by incomplete combustion. As sophistication of methods developed, more than 90 synthesized by-products were estimated which were either polynuclear aromatic hydrocarbons or oxygen-containing derivatives of them, the latter being both carboxylic acids and alcohols. The most recent efforts, illustrated by Figure 15, indicate that some components originally thought to be present in the mixture may not, in fact, be a part of it. Thus, identification by increasingly precise methods is essential to a complete understanding of the phenomenon of "hydrocarbon synthesis in combustion." This is especially true for the thermodynamic studies now being undertaken of the phenomenon. An earlier attitude--that it was not necessary to characterize all of the variety of by-products--must now be abandoned. More accurate determination of the majority of by-products is necessary, whether or not possible toxicologic manifestations are associated with them.

There is no doubt that these arenes and their derivatives are synthesized in the flame itself. This follows from the fact that the fuels burned were relatively simple hydrocarbons proven to contain none of the arenes. Also, the combustion air was free of such compounds. Undoubtedly many possible schemes could be devised showing the mechanism of formation

of arenes during combustion. That scheme illustrated by Figure 2 is one which is adapted from the literature on pyrolysis by Kinney and Crowley [11]. It is generally assumed in such studies that intermediate free radicals participate in the mechanism. It is our present feeling that clarification of the over-all thermodynamics will provide insight into the possible intermediate steps of synthesis.

Although temperature and pressure conditions can be established for optimum yields of arenes, the diffusion flame is far from such an optimum system. As a result, the yield of arenes is very small compared to the 25 to 50% of theoretical yield which has been produced under controlled conditions of pyrolysis. The maximum collection of total extractable organics from poor combustion in the laboratory was in the order of milligrams per gram mole of fuel burned. Only a portion of the total particulate material from either laboratory experiments or from air samples consisted of synthesized hydrocarbons. The remainder, at least from the laboratory burning, was presumed to be carbon. Table IV shows the extractable proportion of the weight of several samples from different fuels. The amount varied from about 38 to 7% in experimental runs. Two air samples similarly treated contained 20 and 12% extractable organics. While both of these air samples fell within the experimental limits, we have heard of some as high as 51% extractable from a coal-burning community.

Table IV shows no clear trend of a tendency of fuels to produce organics when burned in a diffusion flame without primary air. The compound 1-butene, which smokes copiously, produced only a slightly higher proportion of organics to soot than did natural gas, which typically burns very clean. Although the liquid fuels generally produced higher proportions of organics than did the gaseous fuels, one of them (cyclohexane) gave the smallest proportion of all. Additional discussion of air contaminating tendency of various fuels will be found in Appendix A.

No simple technique has been devised for estimating the total arenes or total soluble organics from the particulate by-products of combustion. As a rough estimate only, the color intensity of the extract which is red to reddish-brown provides some indication of the concentrations of arenes and their derivatives.

TABLE IV

PROPORTIONS OF EXTRACT TO SOOT FROM INCOMPLETE COMBUSTION

Fuel	Burning in Furnace[a]	
	Secondary Air / Fuel wt. / wt.	Extract / Soot wt. / wt.
Natural gas[b]	25.0	$\frac{1}{8.4}$
1-Butene[b]	25.0	$\frac{1}{7.7}$
Hexane	17.6	$\frac{1}{4.3}$
Cyclohexane	16.6	$\frac{1}{15.5}$
2,2,4-trimethylpentane	17.3	$\frac{1}{4.1}$
1-Hexene	17.1	$\frac{1}{4.0}$
Toluene	15.9	$\frac{1}{4.4}$
Benzene	15.8	$\frac{1}{9.3}$
Gasoline (50 octane)	16.8	$\frac{1}{2.6}$
Air Sample (Nov 56)	---	$\frac{1}{8.2}$
Air Sample (Dec 56)	---	$\frac{1}{5.1}$

[a]All combustion in the same burner. [b]Gaseous fuels.

It is noteworthy that atmospheric samples taken on days of noticeable air contamination contained the same range of chemicals as those found experimentally in the laboratory. This is illustrated in Figure 6, where the circular chromatogram from one air sample is compared with several known arenes, and with the effluents from an incinerator and the combustion of natural gas. It is not certain what changes may occur in the arenes while they are air-borne in the outdoor environment. Laboratory handling of the polyaromatic hydrocarbons and the chromatograms thereof has demonstrated that many arenes are subject to oxidation or other chemical modification when exposed to air and sunlight. Experience described in connection with analytical procedures (Figure 18) illustrates the effect of ultraviolet irradiation on anthracene and on benzo[a]pyrene. Concerning the apparent reduction in amount of these compounds on repeated instrumental exposure, it was thought to be due to a partial oxygenation of the hydrocarbons to photoxides. This oxygen addition would destroy the resonating system necessary for fluorescence. Whether the arenes adsorbed onto carbonaceous smoke particles in air are similarly affected is unknown at this time. Further study of the question is anticipated because of its obvious significance in contaminated air environments.

Simple diffusion flames have been used in this laboratory for experimental purposes. An ultimate goal of the project is to determine the characteristics of flames and of combustion in general which lead to the production of arenes or which tend to eliminate them from the by-products. In general, it has been found that a hot blue flame is practically free of filterable organic by-products; whereas any tendency of the flame to show a yellow tip will be accompanied by formation of some arenes. It has been noted occasionally, however, that even with apparent complete combustion, minute quantities of pyrene are found by fluorescence on a paper chromatogram. Pyrene appears to be one component having a very high fluorescent efficiency, so that its presence in minute quantities is easily detected; therefore, it is possible that other components are simultaneously present but unnoticed, even in what would be considered complete combustion. Some fluorescent and chromatographic characteristics of a number of the arenes are shown in Table II.

The public health implication of arenes is not solidified, but the major concern is with several which are known experimental carcinogens. It was because of this known carcinogenicity that efforts were made

by sublimation to separate relatively large quantities of such materials as benzo[a]pyrene, dibenz[a,h]anthracene, and others. Biologic assay of such components from contaminated air is now under way in other laboratories. In this connection it is worth noting the similarity between arene-type hydrocarbons and their derivatives found in contaminated air, in smoky effluents from combustion of fuels, and in tobacco smoke. These similarities have been tabulated recently by Sawicki, et al. [12]. In our estimation, the principal difference between the incomplete combustion of tobacco and that of the types of fuels with which we have experimented is that tobacco contains some proportion of nitrogen and sulfur, compounds of which may appear in the effluent. It has been our experience that sulfur- and nitrogen-containing particulates are detectable in outdoor air samples. In only one laboratory sample produced by our techniques was a nitrogen-containing particulate material detected. This was from the incomplete combustion of a low octane gasoline. It was assumed that nitrogen was present in the raw fuel which was less refined than the other experimental fuels used.

If, indeed, the air contaminating characteristics of polynuclear aromatic hydrocarbons are sufficient to cause a health concern, then other criteria of complete and incomplete combustion than those presently accepted in standard mechanical engineering practice are necessary. A gross chemical balance between carbon, hydrogen, and oxygen input and output from a burner is not sufficiently sensitive to observe differences which enter into the formation of the minute quantities of arenes observed in some instances. Certainly the use of a Ringelmann chart for limitation of smoke output from combustion admits of the presence of arenes in some amount, since the usual specification by this criterion is for some allowable density of black carbonaceous smoke.

As mentioned earlier, only one aldehyde from combustion (formaldehyde) was found. Although the analytical procedure was less adequate for higher molecular weight aldehydes, their apparent total absence led to the strong impression that negligible amounts of other members of this group were produced by either incomplete or complete combustion. It was further observed that from several outdoor air samples only formaldehyde could be identified. Of interest was the fact that samples obtained during periods of low outdoor humidity contained relatively large quantities

of formaldehyde. By contrast, those obtained from relatively humid environments contained very small amounts.

In laboratory experiments with methane, propane, and 1-butene. burned inlivi̇dually in flames that varied from incomplete to complete combustion, it was determined that the amount of formaldehyde produced was a function of the amount of secondary air supplied to the combustion system. The pertinent data are shown in Table V. It should be noted that the difference between incomplete and complete combustion was defined by the absence or use of primary air. In all cases sufficient air was available for complete combustion. Figure 19 is a schematic representation of the phenomenon noted, namely, that in the absence of primary air, formaldehyde production diminishes with increasing secondary air. By contrast, when combustion appears complete as primary air is made available, formaldehyde formation increases with increasing secondary air. This effect was considered to result from both cooling of the flame mantle by larger quantities of air and more rapid transport of partially oxidized fuel out of the thermally active zone.

Further, and more detailed studies including related phenomena, are warranted and should be considered. Our own present and projected investigation of the thermodynamics of arene production is related and, in fact, partially instigated by these observations. The possible significance of the formaldehyde phenomenon is that the use of a large secondary air supply to control smoke from combustion may lead to increased emission of other contaminants by modification of thermal zones in flames. It seems quite evident from a variety of studies that a large array of organic chemical entities exists as intermediates or as synthesized products in the combustion process. Conditions which lead to their complete oxidation, or conversely to their emission in the stack gases, need definition if criteria for combustion to minimize air contamination are to be rigorously established.

TABLE V

EFFECT OF SECONDARY AIR ON ALDEHYDE PRODUCTION

Fuel	Run	Air Volume, cu ft		Total Aldehyde Production	
		Primary	Secondary	mg	ppm[a]
Methane, 14 g[b]					
Complete combustion	1	7.8	7.8	1.03	1.7
	2	7.8	11.7	3.14	4.1
	3	7.8	15.6	7.8	8.5
	4	7.8	19.5	13.[illegible]	[illegible]2.4
Incomplete combustion	5	---	15.6		15.7
	6	---	11.7	[illegible]	[illegible]
	7	---	7.8	16.4	[illegible].0
	8	---	4.7	24.5	120.0
Propane, 10 g[b]					
Complete combustion	1	7.8	7.8	0.20	0.3
	2	7.8	11.7	0.56	0.8
	3	7.8	19.5	3.07	3.0
Incomplete combustion	4	---	14.4	1.47	2.6
	5	---	9.6	2.12	5.8
	6	---	5.8	15.3	67.5
1-Butene, 11 g[b]					
Complete combustion	1	7.8	7.8	0.19	0.3
	2	7.8	11.7	1.25	1.7
	3	7.8	15.6	4.45	5.0
	4	7.8	17.6	7.22	7.5
Incomplete combustion	5	---	9.6	8.75	23.7
	6	---	5.8	19.2	85.3

[a]Volume of formaldehyde per million volumes of stack effluent.

[b]Approximate weight of fuel burned per run of one-half hour's duration.

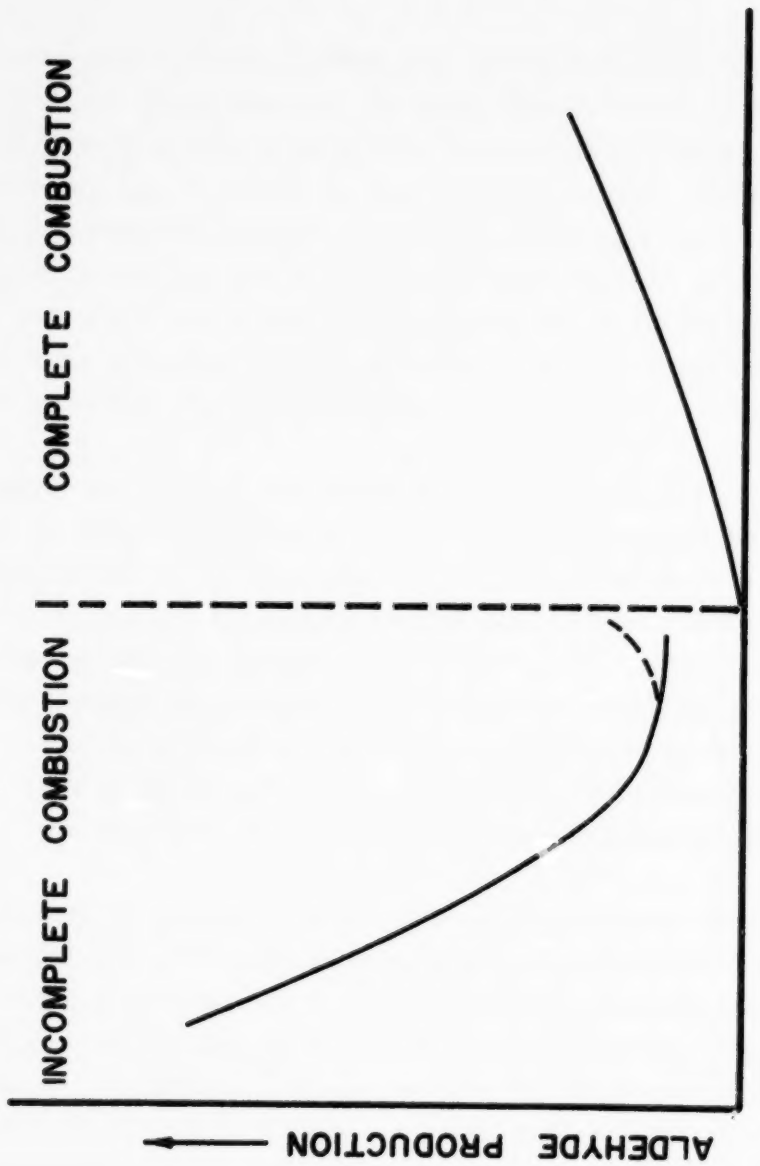


FIGURE 19. EFFECT OF SECONDARY AIR ON ALDEHYDE PRODUCTION

IX. SUMMARY AND CONCLUSIONS

Undoubtedly the most widely used chemical process in modern civilization is combustion of organic fuels for heat and power. In urban areas, where intensive utilization of this process occurs, combustion is cited as a principal source of air pollution. Even excluding secondary reactions which occur photochemically in the outdoor atmosphere, there is an enormous variety of organic by-products from this ubiquitous process. During an investigation of the combustion process it was found that these organics result from both oxidative degradation of fuels and synthesis of complex molecular species occurring simultaneously when combustion is incomplete.

Synthesis is demonstrated by the fact that polynuclear aromatic hydrocarbons with molecular weights up to 300 may be derived from incomplete combustion of such a simple fuel as methane. These hydrocarbons are part of the solid phase of combustion by-products and may be filtered from gaseous components. Among them are the arenes naphthalene, anthracene, pyrene, benzo[a]pyrene, dibenz[a,h]anthracene, and others. Additionally, there exist relatively nonvolatile oxidation derivatives such as alpha- and beta-naphthol, etc. Only a few of the ninety or more individual chemical entities found in these series have been positively identified.

Sufficient evidence exists from burning a variety of gaseous, liquid, and solid fuels to state categorically that it is the process of combustion rather than the chemical quality of the fuel which leads to synthesis of these arenes. Fuels studied include natural gas; propane; butane; 1-butene; 1,3-butadiene; ethyne; hexane; iso-octane; cyclohexane; 1-hexene; benzene; toluene; and gasoline, as well as the miscellaneous celluloses involved in incineration of paper, wood, tree trimmings, etc. The same range of aromatic hydrocarbons have been separated from contaminated air in distressed urban atmospheres.

Investigation of aldehydes produced by combustion indicated formaldehyde to be the only one present in sufficient quantity to permit identification. With availability of sufficient primary air as a criterion

of complete combustion, the amount of formaldehyde decreased with increasing secondary air when combustion was incomplete. However, with complete combustion, use of additional secondary air was accompanied by an increasing quantity of formaldehyde. Thus, using large excesses of secondary air to control smoke may be contraindicted for air pollution control.

The total amount of arenes produced depends in part on the incompleteness of the burning process. While one would assume then that the "smoking point" of fuels would be an index of relative ease of combustion and, therefore, of relative desirability of fuels for urban usage, another possible index, the production of combustion nuclei, is suggested. Such a criterion may become significant in choosing fuels suitable for use in urban environments.

Continuous monitoring of air-borne particulates at one location in the San Francisco Bay Area strongly indicates that during daylight hours, the quantity of particulates is influenced primarily by meteorologic variables, and that an average diminution on week ends relates to variation in fuel usage.

APPENDIX A

COMBUSTION NUCLEI

As an adjunct to the principal interest of this project, attention has been given to the air contaminating potential of several gaseous fuels. While fuels have different tendencies to produce smoke when burned in a specified manner (smoking point), a more significant criterion for their contribution to air quality may be the relative ease of their production of combustion nuclei [13]. Experimental evidence showed that the relative order of increasing air pollution potential of several gaseous fuels on this basis was: methane, ethene, ethane, propane, propene, 1-butene, 2-butene, butane, 1,3-butadiene, and ethyne.

Observations were made with a photoelectric nuclei counter on the effluent from the fuels burned individually in a laminar diffusion flame supplied with a constant rate of clean secondary air. Less than 10^2/cc nuclei were present in both fuel and air supplied to the burner. The counter was a cloud chamber type so arranged that water supersaturation of at least 350% was created for condensation on nuclei. To provide nuclei concentrations within the transmission range of the light source and photometer system, some samples were diluted with clean air. More detailed description of the entire system may be found in Reprint 13.

Table VI shows the relative rates of fuel combustion at which an arbitrarily chosen concentration of nuclei (2×10^5/cc) was produced. From preliminary experimental data on coagulation rates of nuclei, this concentration was selected as being a point of incipient carbon formation. For practical purposes emissions of nuclei below this concentration were considered to be relatively nuclei-free. It was found that all fuels when burned at higher rates produced rapidly increasing numbers of nuclei. With some gases, for example, 1,3-butadiene, visible smoking commenced at only slightly higher fuel flow rates. By contrast, in the case of butane, the nuclei-free fuel flow rate was 16.5 cc/min while smoking occurred at 59 cc/min.

Notable from Table VI is the fact that methane, as anticipated, was the cleanest burning fuel, and that in general the relative ease of

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production of nuclei increased with increasing molecular weight and with increasing unsaturation of the fuel. This observation basically agrees with generalizations on smoking tendency. However, as indicated, the actual production of smoke is not clearly related to its incipient production as defined by this nuclei-free scale.

TABLE VI

RELATIVE MAXIMUM NUCLEUS-FREE FUEL RATES

Fuel	Q_m, cc/min	$1/Q_m$ [a]	$\frac{(Air)\,s}{(Air)\,st}$ [b]
Methane	178.0	0.562×10^{-2}	1.36
Ethane	37.0	2.70	3.73
Propane	25.5	3.92	3.79
Butane	16.5	6.06	4.50
Ethene	50.5	1.98	3.18
Propene	25.5	3.92	4.20
1-Butene	19.0	5.26	4.24
2-Butene	19.5	5.13	4.13
1,3-Butadiene	15.5	6.45	5.66
Ethyne	4.0	25.00	48.30

[a] Fuel flow when nucleus concentration in effluent equals 2×10^5 cc. Q_m reported to nearest 0.5 cc/min except for methane.

[b] Ratio of volume of air supplied to volume of stoichiometric air for complete combustion.

If, in fact, the availability of an excess of nuclei in the outdoor environment leads to coagulation and growth of particles, such manifestations as atmospheric heterogeneity associated with deteriorated air quality may be controllable only by limiting nuclei emissions. Selection of fuels using as rigorous a criterion as that indicated here may become a significant part of air quality control.

APPENDIX B

CONTINUOUS AIR MONITORING

An associated, though separately supported set of observations, has resulted from the continuous monitoring of air for particulates with the AISI Smoke and Fume Sampler [14, 15, 16]. For more than eight years, almost continuous sampling with this device at one location has served to delineate certain trends of air quality in Berkeley, California. The device draws air at about 0.25 cubic feet per minute through filter paper with a fresh 1-inch diameter spot exposed every two hours. The obscuration due to the deposit is measured with a transmission densitometer, and the results are interpreted in COH (coefficient of haze) units per 1000 linear feet of air filtered. No chemical analysis of these samples has been assayed.

Although densitometry is exponential when used directly, conversion to the COH unit makes the latter approximately linear so that direct comparisons among the numbers are possible. Through the total monitoring period there has occurred a diminution in particulate contamination at the sampling site. This is demonstrated by the following array which is the average COH for each of eight consecutive years: 0.71, 0.76, 0.71, 0.54, 0.69, 0.59, 0.56, and 0.55. This downward trend, at least during the past four years, may have been caused by increasing the intensity of control activities in the San Francisco Bay Area. Most community-wide control during this period has been directed at particulate emissions from both open burning of rubbish and from a variety of industrial and commercial combustion and manufacturing processes.

Substantiating this possibility is the fact, repeated each year, that week ends, and especially Sundays, are freer of particulates than mid-week days. Graphical representation of this phenomenon is shown in Figure 20, for the first five years; the same pattern has continued to the present date. To the extent that particulate emissions from industry, commerce, and other activities are reduced by the week-end shutdown, this weekly diminution reflects the equivalent of control activities.

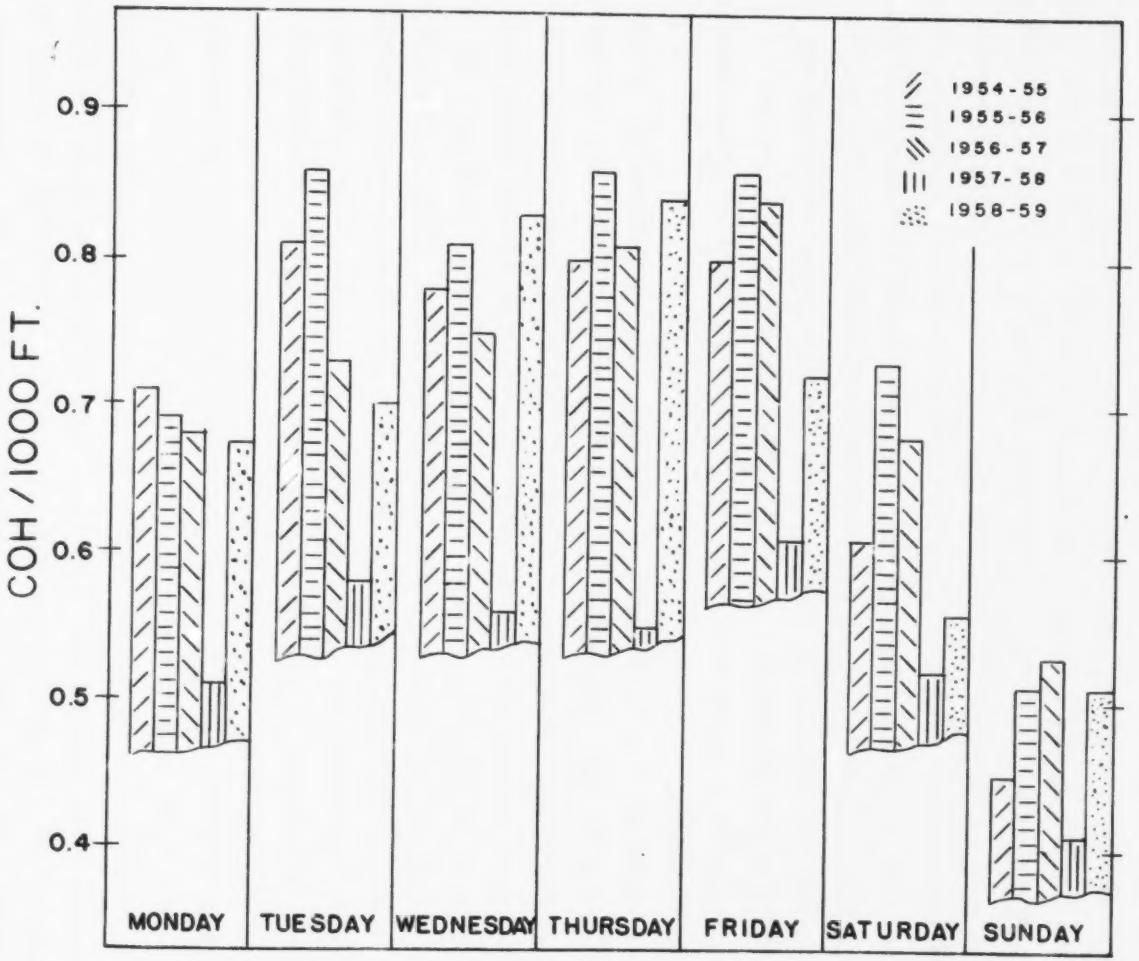

FIGURE 20. AVERAGE ANNUAL PARTICULATE POLLUTION BY HOUR OF THE DAY

Evidence that the apparent gradual decrease of particulates is not related to automotive transportation is the contrasting regular increase of accurately counted traffic on the San Francisco-Oakland Bay Bridge. During annual periods coinciding with the monitoring, automobile passages increased from 3 to 6 per cent per year and truck passages from 1 to 7 per cent. In no period was there a decrease; over the full eight years of monitoring, passages of automobiles increased 29.4% and of trucks 22.3%. By contrast, the particulates filtered from the air were about 22% lower in the eighth than in the first year of observation.

The months having highest levels of filterable contamination were November and December, with April and May usually lowest. The following tabulation shows the average by month of the full eight years' data:

May	0.42	November	1.07
June	0.47	December	1.20
July	0.45	January	0.92
August	0.50	February	0.56
September	0.57	March	0.44
October	0.70	April	0.39

The reason for this is probably meteorological. Records show the lowest average wind speed in November and maximum velocity in July. Other large-scale phenomena are similarly variable in different seasons. One fact which tends to show at least that domestic heating practice (almost exclusively by natural gas in this area) is less important than meteorology in the community's air contamination is that the heating requirements are about equal in April, May, and November, the months of almost maximum contrast in air quality as measured by filterable particulates.

Comparison of average contamination in Berkeley and in a few communities of the Eastern United States by the same method shows relatively low particulate loadings here where solid fuels are practically unused.

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